PB83-187443

Organic Compounds in Surface Sediments and Oyster Tissues from the Chesapeake Bay

Virginia Inst. of Marine Science
Gloucester Point

Prepared for

Environmental Protection Agency
Annapolis, MD

Apr 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-187443

EPA-600/3-83-018a
April 1983

ORGANIC COMPOUNDS IN SURFACE SEDIMENTS AND OYSTER TISSUES FROM THE CHESAPEAKE BAY

by

R. H. Bieri, P. DeFur, R. J. Huggett, W. MacIntyre,
P. Shou, C. L. Smith, and C. W. Su

Virginia Institute of Marine Science
and School of Marine Science,
College of William and Mary
Gloucester Point, Virginia 23062

Grant
R806012

Project Officer

Duane Wilding
Chesapeake Bay Program
2083 West St., Suite 5G
Annapolis, MD 21401

CHESAPEAKE BAY PROGRAM
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ANNAPOLIS, MD 21401

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC INFORMATION

PB83-187443

Organic Compounds in Surface Sediments and Oyster Tissues from the Chesapeake Bay,

Apr 83

R. H. Bieri, P. DeFur, R. J. Huggett, W. MacIntyre, and P Shou.

PERFORMER: Virginia Inst. of Marine Science, Gloucester Point.
Grant EPA-R-806012

SPONSOR: Environmental Protection Agency, Annapolis, MD.
Chesapeake Bay Program.
EPA-600/383-018A

See also PB83-187450. Prepared in cooperation with College of William and Mary, Williamsburg, VA.

The objectives of this study were to determine the identity and quantity of toxic organic compounds within the Chesapeake Bay, to delineate their spatial and temporal distribution and to point out existing problem areas.

KEYWORDS: *Organic compounds, *Sediments, *Chesapeake bay, *Tissues(Biology), *Chemical analysis, *Water pollution detection, *Water pollution sampling.

Available from the National Technical Information Service, Springfield, Va. 22161

PRICE CODE: PC A09/MF A01

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Grant No. R806012 to College of William and Mary, Annapolis, Maryland. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER
TYPING GUIDE SHEET

EXECUTIVE SUMMARY

The objectives of this study were to determine the identity and quantity of toxic organic compounds within the Chesapeake Bay, to delineate their spatial and temporal distribution and to point out existing problem areas.

The following pages provide a short summary of our efforts. For a more detailed description, the main text should be consulted.

METHODOLOGY

A. Sampling

A basic difficulty with any monitoring program which is intended to assess the state of a body as large as the Chesapeake Bay is in the selection of the sample type and sample location. Ideally, one would like to obtain and analyze enough "pieces" of the ecosystem, so that any spatial and temporal abnormalities could be detected. Unfortunately, with time and financial constraints, the ideal case is not achievable. Therefore one must carefully select what and where to sample in order to be as efficient as possible and to still obtain data which reflect the state of the area being assessed. We selected bottom sediments and oysters. The former were chosen because of the usually high preference that synthetic organic compounds show for concentrating in and on sediment particles. Kepone in the James River is an example of this. While dissolved concentrations in the water were in the low parts per trillion range, Kepone levels in the bottom sediments were more than a thousand times higher. The affinity of synthetic organics for sediments yields two major benefits: (1) the compounds of interest are present in relatively high concentrations, thus making the analysis simpler and (2) the sediments accumulate the foreign materials over long periods of time thus integrating and making the detection of pulsed inputs more likely. Oysters were selected because they share the two advantages of sediments listed above as well as being organisms, thus serving as a link to the biota of the Bay. They are also sessile. Being sessile is an important consideration in interpreting the data. Since the animal moves little (if at all), a compound detected in an oyster sample assures that the animal received it at the sampling location. This is not necessarily true for mobile organisms like fish or crabs.

Sample locations were then selected. We gave prime consideration to the areas of the Bay which were expected to contain fine grained sediments since these usually accumulate higher levels of organic compounds than do more coarse ones under similar exposure. We also considered areas which would have the highest probability of reflecting man's activities. These included the mouths of the major tributaries and zones of high urban and industrial activities. The oyster sample locations were chosen as near as possible to the sediment sample locations. The locations are given in Figures 1 and 2. To get an indication of temporal trends, these stations were sampled twice during 1979, once in the spring and once in the fall.

B. Analytical Techniques

In brief, the methodology involves first freeze drying of the sample to remove moisture and thus providing better penetration of the extracting solvent into the sample matrix. This in turn allows for a higher extraction efficiency. The dried sample is then Soxhlet extracted with methylene chloride. After this step the extract, containing not only pollutants of interest but also many natural compounds, must be fractionated. There are two steps in the fractionation. The first utilizes Gel Permeation Chromatography to remove high molecular weight compounds which are probably biogenic or natural. The remainder is then split into three parts by High Performance Liquid Chromatography. One fraction is aliphatic and alicyclic in nature, one is mainly aromatic and the third contains polar compounds.

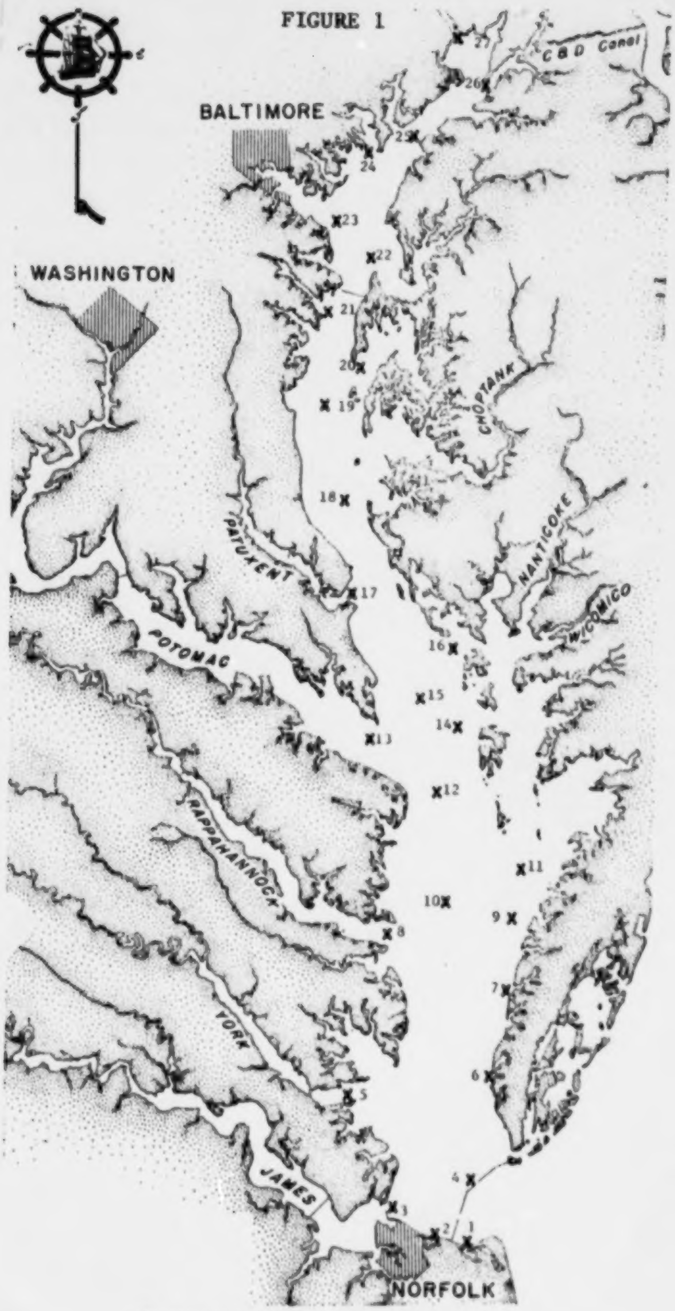
The "aromatic" fraction has received the most study in our project since it is likely to contain most of the toxic organic compounds. The polar fraction of samples from the Bay contained very few compounds and most were at low concentration, so that little effort was expended on it. The aliphatic/alicyclic fraction was not extensively studied since most of these compounds are of relatively low toxicity. Indications of oil pollution can be obtained from aliphatic as well as from the aromatic compounds. Therefore, for the sake of efficiency, the aromatic fraction was the subject of the greatest effort.

After extraction and fractionation, the samples were analyzed by high resolution glass capillary gas chromatography and gas chromatography-mass spectrometry, also using glass capillary columns.

The output from the gas chromatographs consists of electrical signals which are proportional to the amount of a compound going through the detector. The time required for a compound to reach the detector (retention time) is a function of the molecular structure of the compound. So, with the intensity of the signal and the time parameter, one obtains both quantitative and qualitative information regarding the concentrations and identities of the compounds.

If one were looking for only a few compounds, such as PCB's and Kepone, then standard solutions of these could be anlayzed and the resulting retention times and intensities compared to those of the sample. Our program, however, is looking for hundreds of compounds, many of which are not known to be present until detected. Therefore, standard solutions containing all compounds of interest are impossible. To characterize these compounds, we have developed and used a relative retention index based on unsubstituted polynuclear aromatic compounds. This index allows the

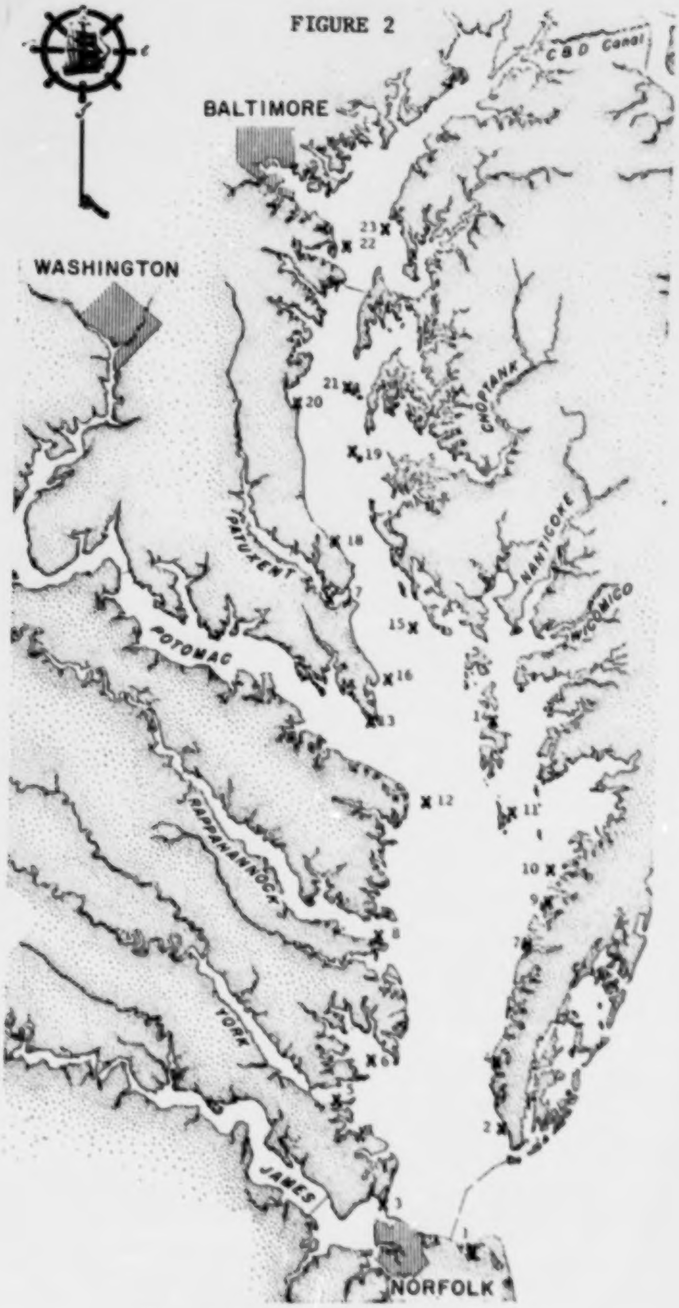
FIGURE 1


BALTIMORE
WASHINGTON
NORFOLK
C & D Canal
CHOPTANK
PATUXENT
NANTICOKE
WICOMICO
POTOMAC
RAPPAHANNOCK
YORK
JAMES
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Chesapeake Bay Sediment Sample Locations

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
2 7/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

FIGURE 2


BALTIMORE
WASHINGTON
C&D Canal
CHOPTANK
NANTICOKE
WICOMICO
PATUXENT
POTOMAC
RAPPAHANNOCK
YORK
JAMES
NORFOLK
23
22
21
20
19
18
17
15
16
13
14
12
11
10
9
8
7
6
5
4
3
2
1

Chesapeake Bay Biota Sample Locations

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
5/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-75)

computerization and storage of Gas Chromatographic data for all peaks in the chromatogram, even though their identity may be unknown. Computer software can be written to compare the content of one sample with others. By knowing the aromatic retention index of a compound, the computer bank can be searched to determine which samples may contain the compound.

Unfortunately, gas chromatography alone is not sufficient to completely analyze samples as complex as those from the Chesapeake Bay. Gas Chromatography-Mass Spectrometry is required to determine a compound's identity based on the intensity of the molecular ion and the abundances and masses of the ion fragments which result when the compound is bombarded with electrons. The same relative retention index used for the gas chromatography is used for gas chromatography-mass spectrometry.

We emphasize that this is a very brief summary of our analytical methodology. The methodology is not without problems and is still being refined. It has, however, been utilized to give the most complete picture of organic pollutants in the Chesapeake Bay ever obtained.

RESULTS

A. Bay Sediments

Analyses of sediment samples collected during the spring and fall of 1979 revealed that over three hundred compounds were abundant enough to be either identified or given a surrogate name by assigning an aromatic retention index. It should, however, be realized that this number is essentialy proscribed by the resolution of the GC column. Thus, the actual number of compounds present in the G32 fraction is much higher as one can see from the resolvable envelope in the chromatogram of Figure 3, but since only chromatographic peaks can be quanitified, it does not make sense to identify mass spectra that occur in valleys between peaks.

To give an indication of the distribution of organic compounds in bottom sediments in the Bay, Figures 4 and 5 are presented. These are bar graphs derived from samples collected in the spring and fall of 1979. Station numbers are indicated on the vertical axis (with their locations given in the chart to the left). The summed concentrations of chromatographically resolvable compounds eluting in the "aromatic" fraction is represented by the length of the bar on a logarithmic scale. Both figures immediately convey the fact that the highest total concentrations are encountered in the northern portion of the Chesapeake Bay and that samples from Stations 2, 4, 6, 7, 10, 11 and 12 in the lower Bay are almost devoid of these compounds. With the exception of the fall sample from Station 9, only samples from locations 1, 3, 5, and 8 contained sums between one hundred and one thousand parts per billion. Stations 1, 3, 5, and 8 were located at the mouths of the Lynnhaven, James, York and Rappahannock rivers respectively.

Unless the sedimentological character of these samples is taken into account, it is risky to assume that these distributions show that the Northern Bay and the river mouths have unusually high levels of organic

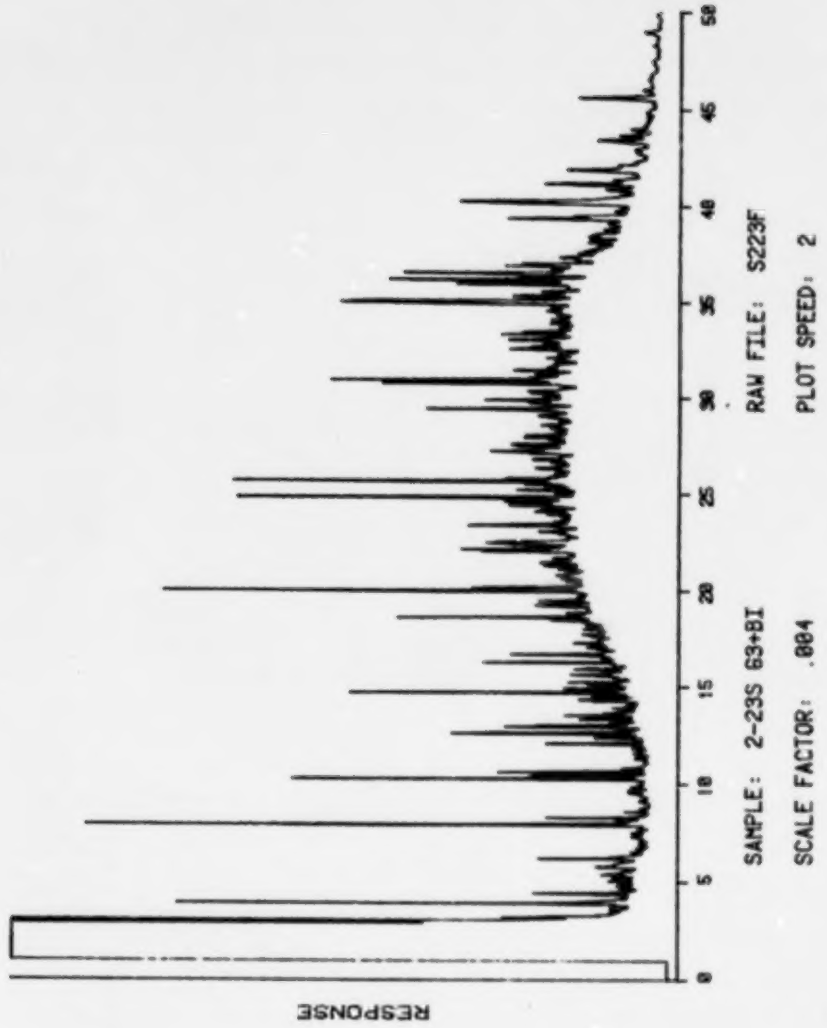


Figure 3. High-resolution chromatogram of "aromatic" fraction (G32) of sample 2-23-S. Note that the number of peaks that can be revolved is limited by the width of individual peaks.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-78)

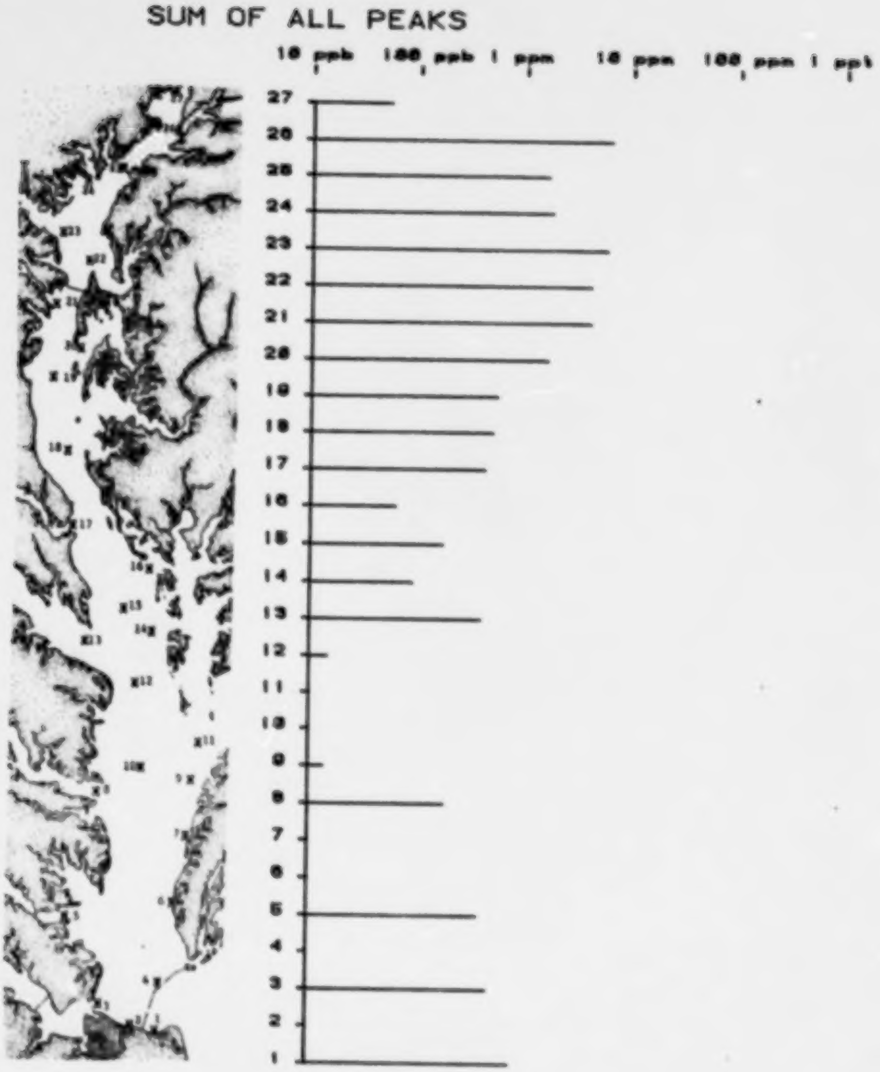


Figure 4. Distribution of organic compounds in surface sediments of the Chesapeake Bay, Spring 1979. The height of individual bars represents the logarithm of the concentration sum of all resolvable peaks. The sample locations are found by locating the numbers to the left of the bars in the map.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.) (9-78)

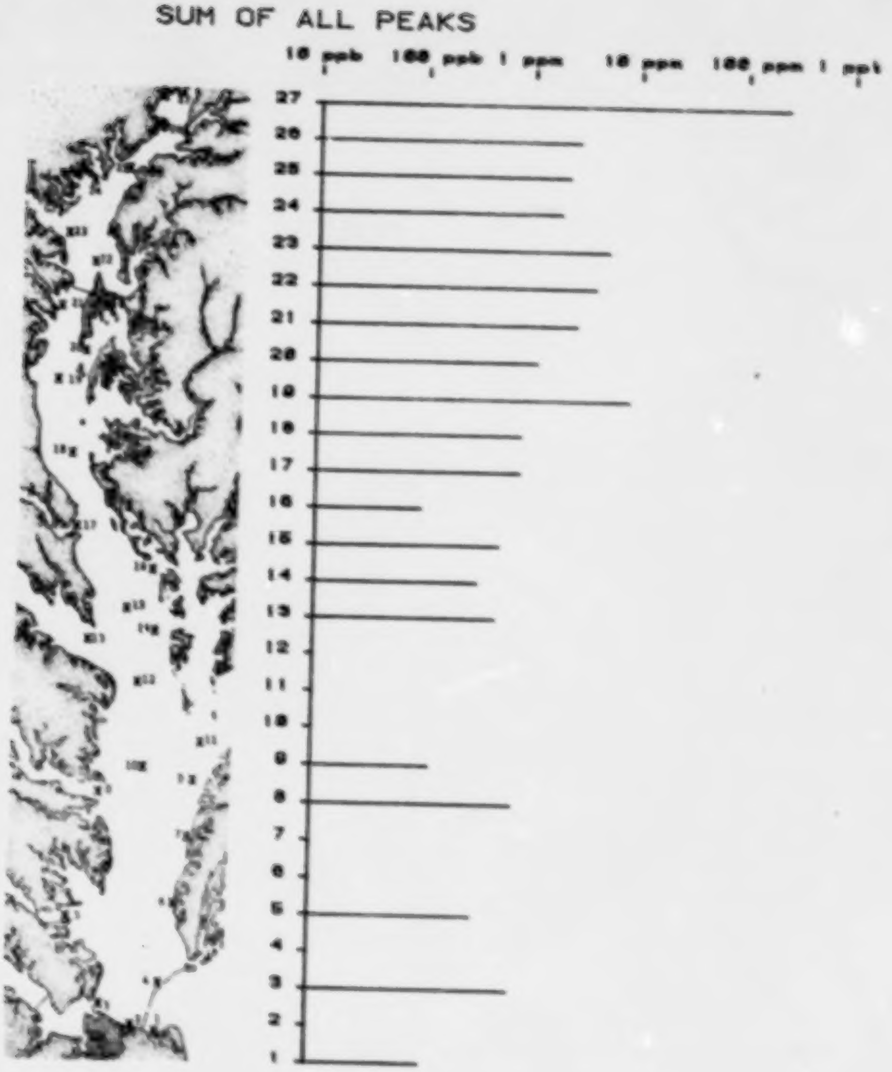


Figure 5. Distribution of organic compounds in surface sediments of the Chesapeake Bay, Fall 1979. The height of individual bars represents the logarithm of the concentration sum of all resolvable peaks.

BOTTOM OF IMAGE AREA (OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS)
BEGIN LAST LINE OF TEXT

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

compounds. As previously mentioned, fine grained sediments are likely to contain higher concentrations of organic compounds than coarse ones and thus affect the distribution of organic compounds. In general, the sediments samples from the Northern Bay and the major river mouths contained a higher fraction of silt and clay than did the other samples. Therefore, to normalize the concentrations of organics to the silt and clay content in the samples seems a reasonable approach to help account for the sedimentological effects. Normalized bar graphs are presented in Figures 6 and 7. There is no substantial change in the concentration sums in the Northern Bay with the exception of Station 27. In the lower Bay only Stations 1, 3, 9, 11 and 12 have visibly increased.

Normalizing the data from the Northern Bay did not substantially change the distribution pattern. With the exception of the sample from Station 19 collected in the fall (this will be discussed later as there was an obvious introduction of pesticides and PCB's here between our samplings), there is an evident trend of increasing concentrations from just below the Potomac River to the mouth of Baltimore Harbor. North of Baltimore Harbor the concentration sums decrease and then increase to another maximum near the mouth of the Chesapeake and Delaware Canal. The most northerly samples, Station 27--inside the mouth of the Susquehanna River--showed considerable variation between samplings. This variation was explained by the flow rates from the Susquehanna which were unusually high prior to the spring sampling and unusually low prior to the fall collection. It can be hypothesized that high flow scours the fine grained particles, but during low flows these materials deposit in the mouth. Therefore, it appears that the Susquehanna River during high flow conditions is a source of organic compounds to the Northern Bay, while the area near or at the mouth may act as a sink during low flow conditions. This source, however, is unlikely to explain the peak concentrations in Figures 4 and 5 near Baltimore Harbor.

Up to this point, the discussion has centered on the concentration sums of all resolvable components. While the total concentration sums allow a judgment of the quantities of organic compounds encountered in the Bay, Figures 8 and 9 give much more relevant information insofar as they represent the concentration sums of a group of compounds that contain many toxic, carcinogenic, mutagenic and teratogenic members, the polynuclear aromatics or PNAs. All of the PNAs whose concentrations have been summed in Figures 8 and 9 are unsubstituted hydrocarbons and known to be generated in high temperature processes. As such, they are likely to be man-made pollutants (Youngblood and Blumer, 1975; Grimmer and Bohnke, 1972; Grimmer et al., 1979; Lao et al., 1975; Lee et al., 1977; Oak Ridge Nat'l Laboratory, 1979).

Although a "natural" origin in forest and prairie fires can be postulated (Youngblood and Blumer, 1975), their obvious preponderance in sediments near large population centers, industrial complexes and dense transportation networks must be taken as evidence of man-made input.

All the trends which were listed for Figures 4 through 7 generally also apply for the PNAs:

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(8-76)

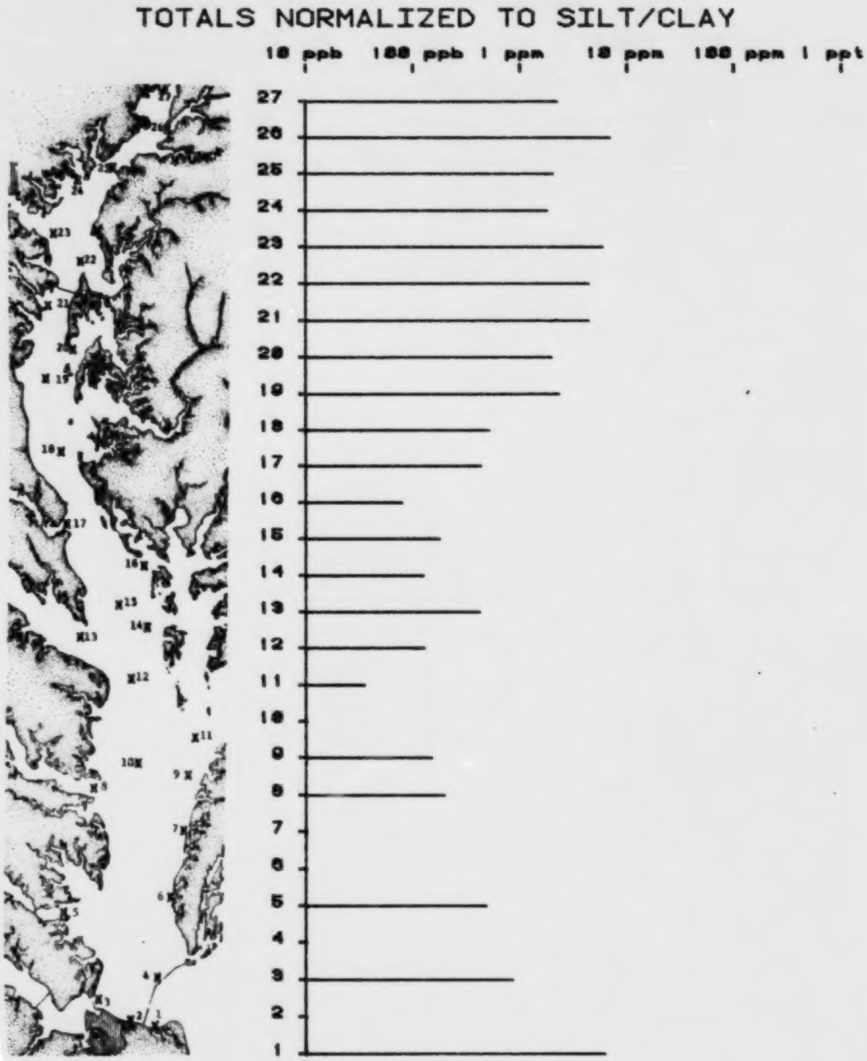


Figure 6. Normalized bar graph of concentration sums of all resolvable peaks in chromatograms of extracts from surface sediments, Spring 1979. This figure is similar to Figure 4, but in calculating concentration it has been assumed that all organic compounds are ad- or absorbed to silt and clay.

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-79)

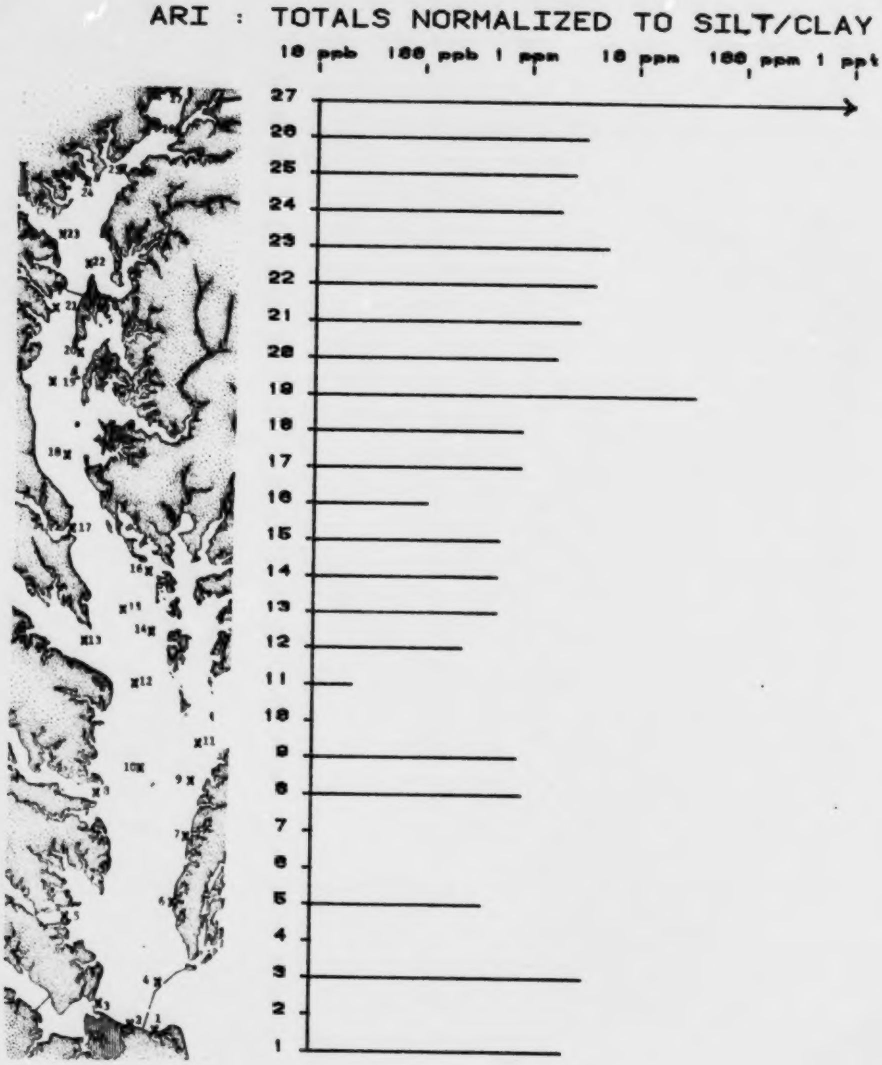


Figure 7. Normalized bar graph of concentration sums of all resolvable peaks in chromatograms of extracts from surface sediments, Fall 1979. This figure is similar to Figure 5, but in calculating concentration it has been assumed that all organic compounds are ad- or absorbed to silt and clay.

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

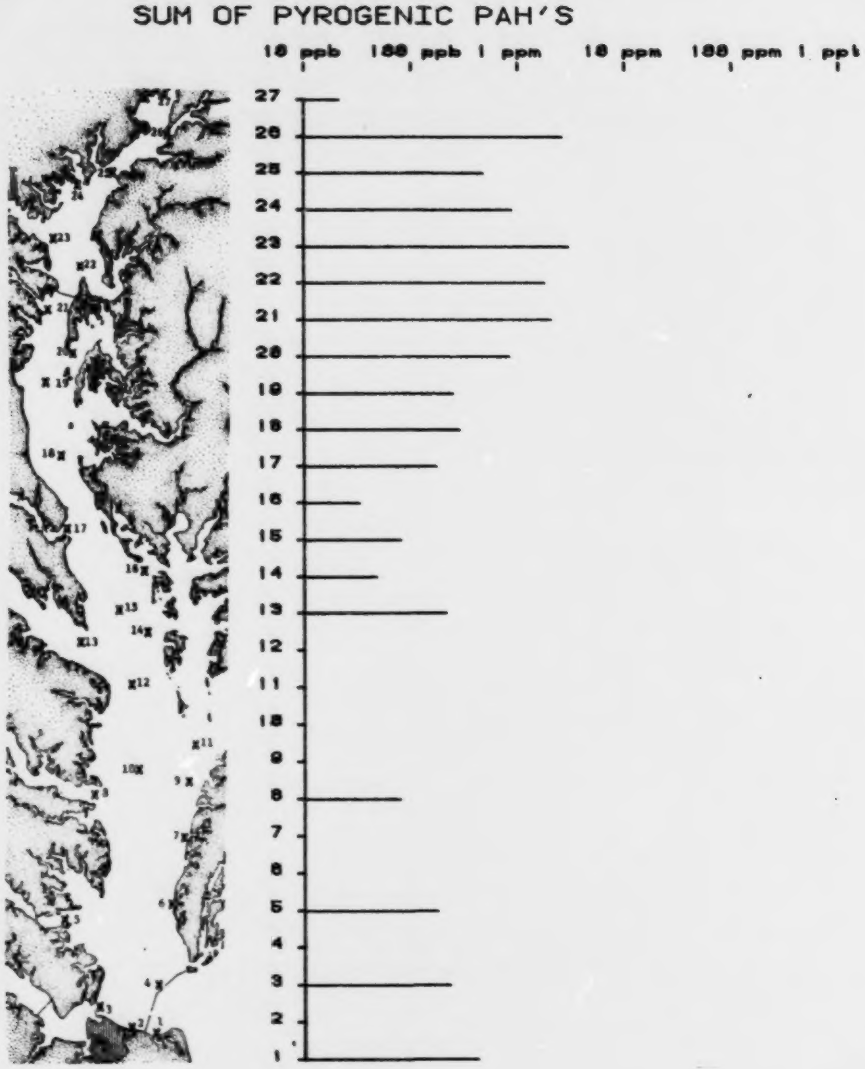


Figure 8. Concentration sums of polynuclear aromatic hydrocarbons in surface sediments, related to the combustion of carbonaceous matter, Spring 1979.

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/2"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

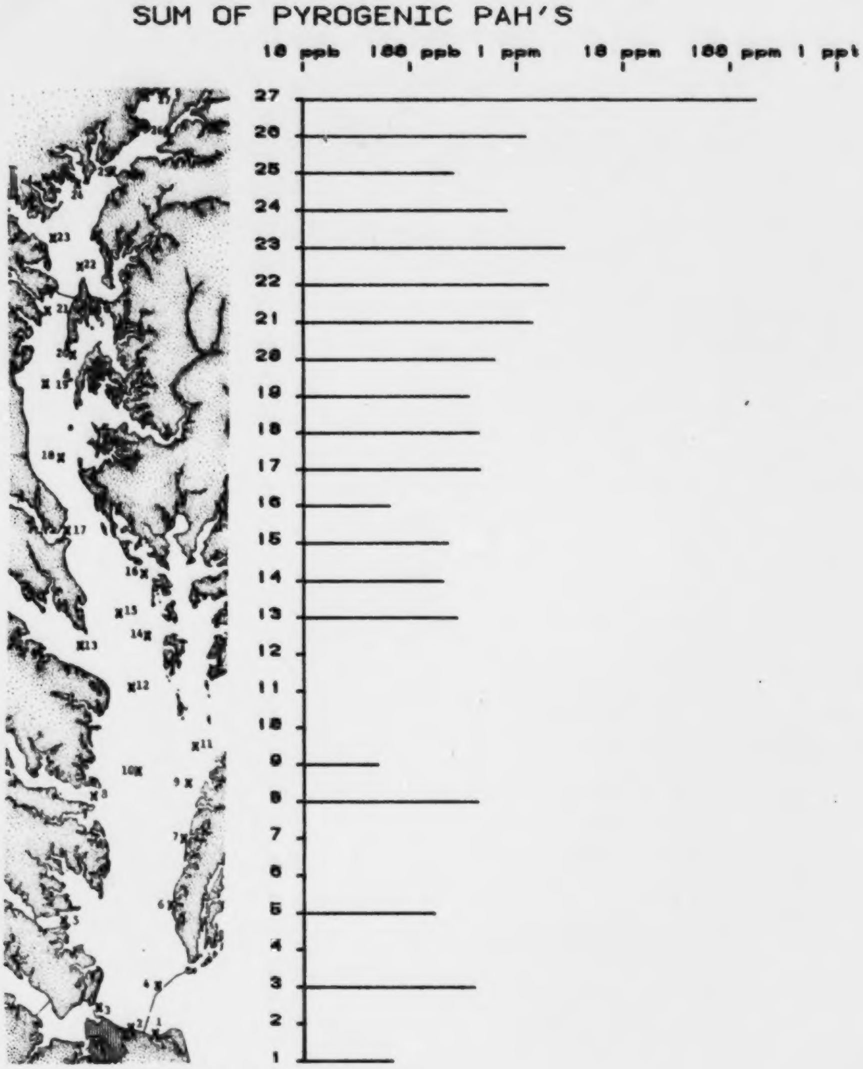


Figure 9. Concentration sums of polynuclear aromatic hydrocarbons in surface sediments, related to the combustion of carbonaceous matter, Fall 1979.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

(a) The concentrations are higher in samples from the Northern Bay.

(b) In the Southern Bay, highest concentrations are found near river mouths.

(c) Concentrations tend to increase from the Potomac River to Baltimore Harbor.

(d) The Susquehanna River mouth sediments show considerable variability but can reach concentrations as high as one part per thousand (normalized to silt & clay).

Bar graphs of two PNAs known for their carcinogenic properties are presented in Figures 10 and 11. Data displayed in these figures show even more clearly that a concentration maximum occurs in the Northern Bay in the vicinity of Baltimore Harbor and strongly suggest that this area is an important source.

The sediment samples collected at Station 19 were unusual in two aspects. One was a large increase in the overall concentrations of organic compounds between the spring and fall samples; the other was a concurrent compositional change. The gas chromatogram for the fall sample was dominated by a very large peak that was identified (by mass spectrometry and retention) to be p,p'-DDT. o,p'-DDT was also present, but the derivatives, p,p'DDE and o,p'-DDE, were not detected. Also present in abundance were polychlorinated biphenyls. Compared to the chlorinated hydrocarbons, the concentrations of PNA's were very small. This was the only sample collected in the Bay in which chlorinated hydrocarbons assumed such an overpowering presence. From the fact the p,p'-DDE and o,p'-DDE, compounds to which DDT would degrade over time, could not be found, one must conclude that a recent dumping operation had occurred. The relatively high PCB levels, not found in any of the other samples, point in the same direction.

In view of the drastic changes in the sample compositon between the two cruises, this station and an area surrounding it were resampled about six and one-half months later (in cooperation with EPA, Annapolis). Analyses indicated p,p'-DDT to be present at levels < 30 ppb.

The changes in sample composition and concentration occurring at Station 19 between the first and the second cruise are likely the result of the dumping of pesticides at high concentration in a container (such as a bag, carton or sheet-metal container) which in time eroded away or was disturbed in the sampling process, thus contaminating the area.

B. Oyster Samples

The gas chromatograms of oyster tissue extracts were much less complex than those of sediments, and the concentration of individual compounds was substantially lower than in sediments. The bar graphs in which the concentration represents the sum of all peaks are given in Figures 12 and

EPA-287 (Cin.)
(4-76)

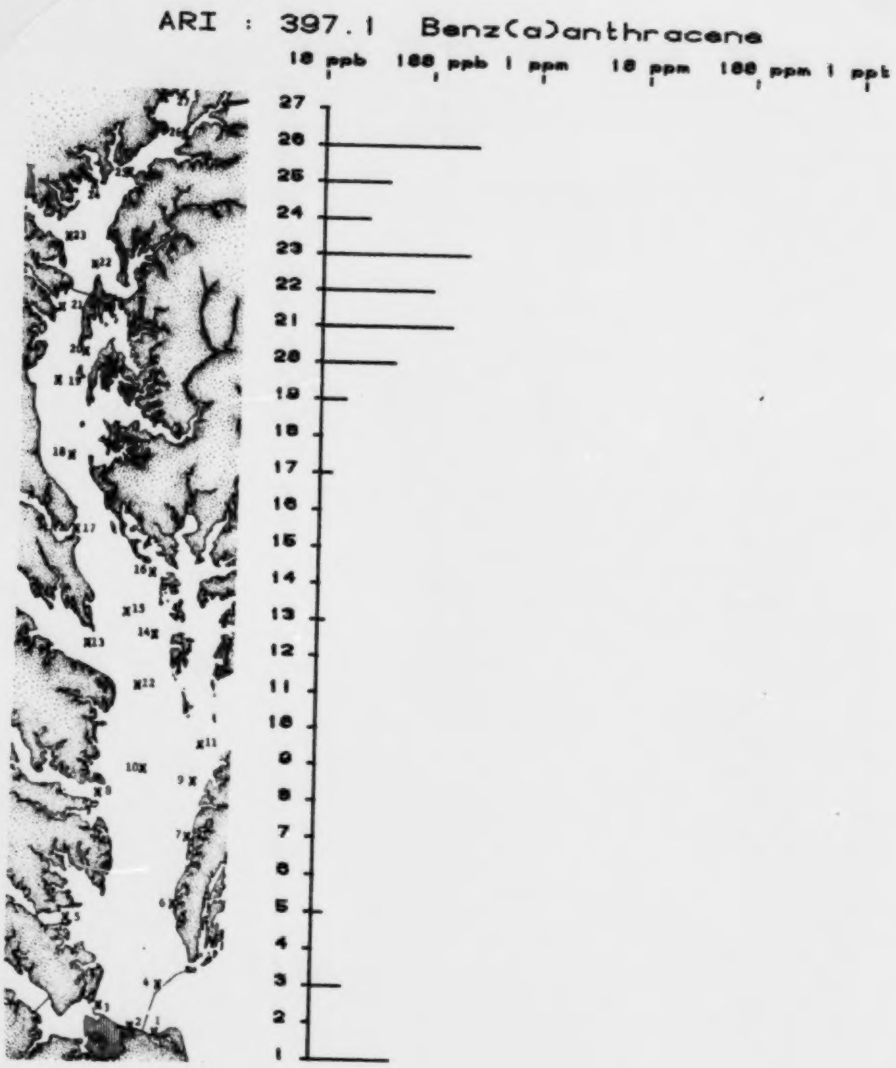


Figure 10. Distribution of benzo(a)anthracene in surface sediments from the Chesapeake Bay, Spring 1979.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

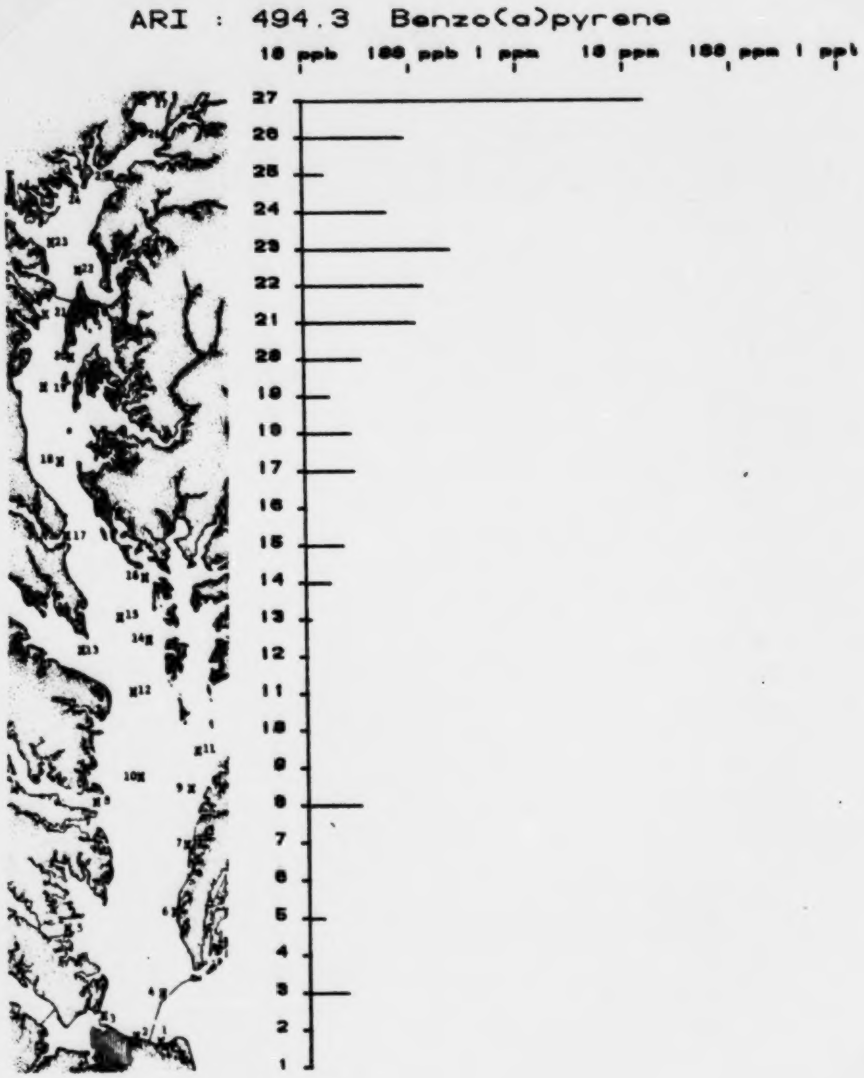


Figure 11. Distribution of benzo(a)pyrene in surface sediments from the Chesapeake Bay, Fall 1979.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

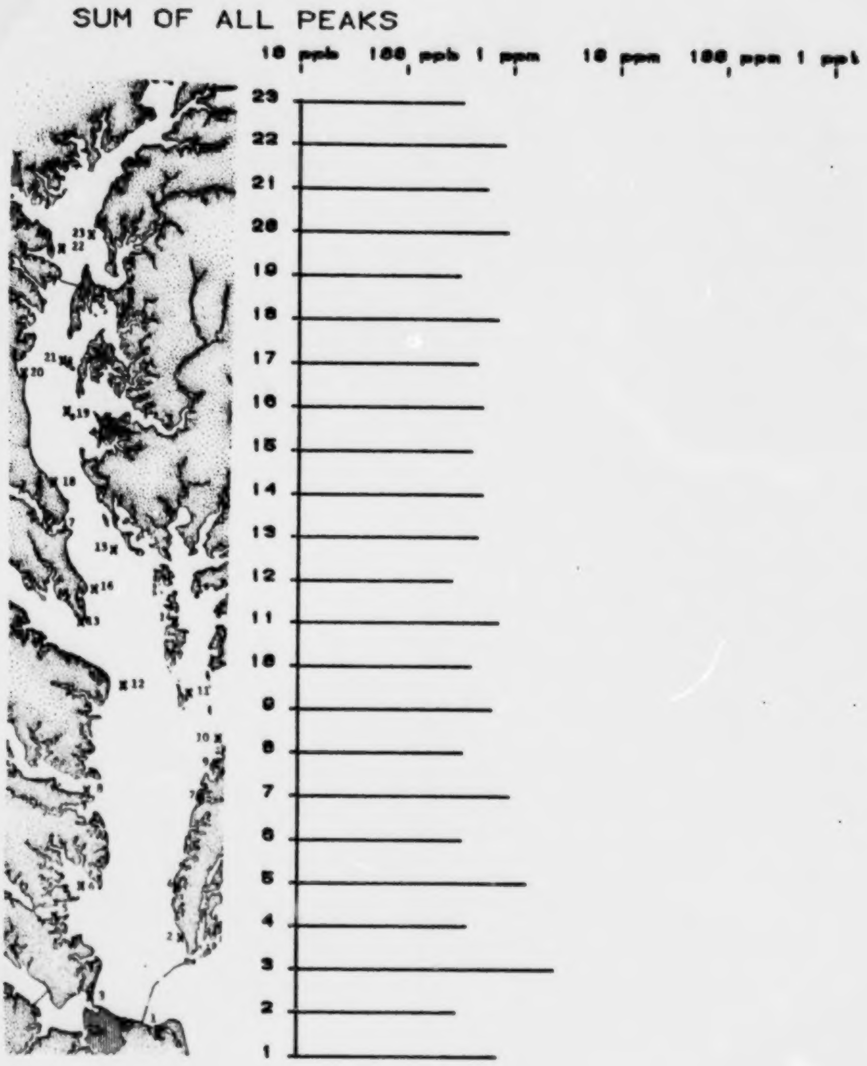


Figure 12. Concentration sums of all resolvable peaks in chromatograms of oyster extracts, Spring 1979.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

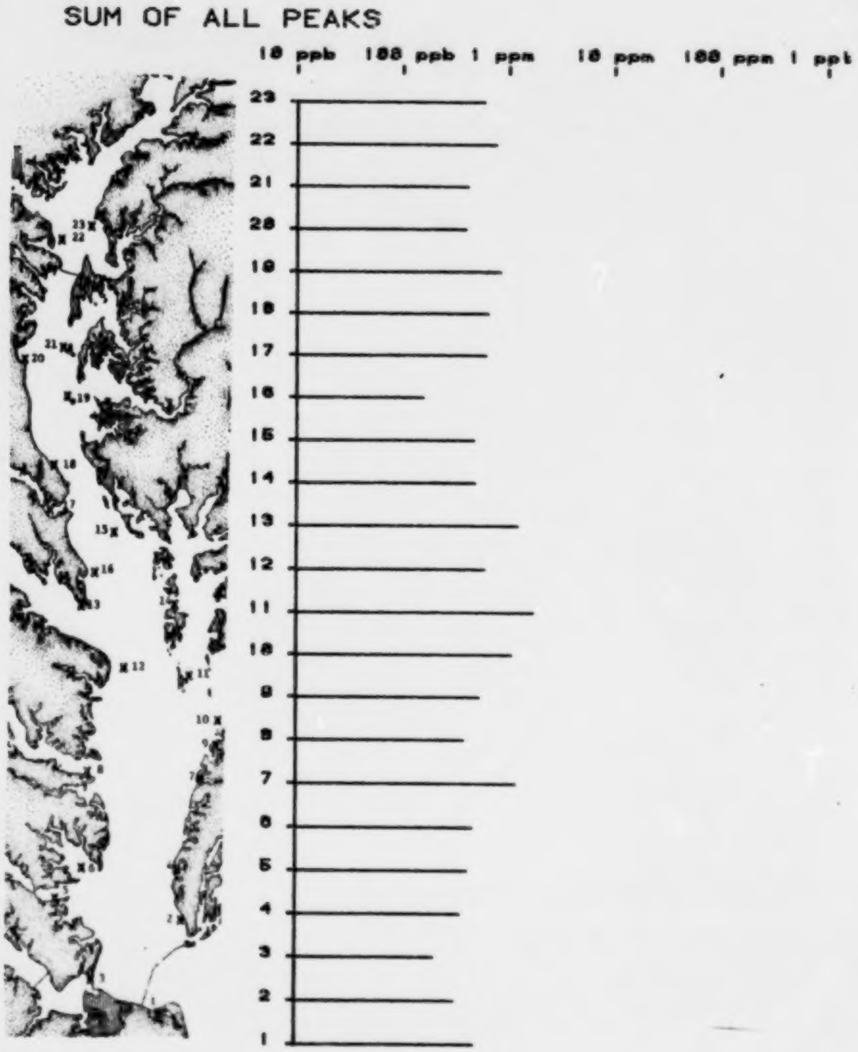


Figure 13. Concentration sums of all resolvable peaks in chromatograms of oyster extracts, Fall 1979.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

13. It is obvious that there are no visible trends simliar to those in the corresponding bar graphs for sediments.

Many of the compounds present had structures we could not identify. In addition, methyl esters of fatty acids were present in most samples, as were some ketones. We hypothesize that many of these compounds have a biogenic or natural origin. Since they are often present in higher concentrations than identified pollutants, the concentration sums may not represent the pollutant content in oysters. Therefore a more meaningful approach may be to examine the number of compounds detected and their spatial distributions. In all, there were 127 compounds tabulated. Oysters collected at the mouth of the James River contained 94 of these compounds. Oysters collected from Station 7 at Occohonnock Creek contained 27 and those from near Baltimore Harbor at Station 22 had 24. The oysters from Station 20 at Holland Point contained 23 compounds and those from Station 10 at Onancock Inlet had 19 compounds.

If only the most concentrated compounds are considered, a similar pattern emerges. There were 42 compounds detected whose individual concentrations exceed 50 ppb. The samples from Station 3 at the mouth of the James River contained 29% of these. The next highest were from Station 22 near Baltimore Harbor with 24%. These were followed by Station 10 with 21%, Station 20 with 17% and Station 7 with 14%. In summary, the following emerges:

(a) From abundance of compounds
    James River > Occohonnock Creek > near Baltimore Harbor > Holland Point > Onancock Inlet

(b) From individual compound concentrations greater than 50 parts per billion
    James River > near Baltimore Harbor > Onancock Inlet > Holland Point > Occohonnock Creek

In both cases the same five stations emerge as being the highest. Also, the James River station is highest in both, and the station nearest Baltimore Harbor is second in one and third in the other.

Comparison of the compounds detected in the oysters with those found in the nearby sediments shows little correlation. In sediment samples the most abundant compounds were PNAs. With the exception of dibenzothiophene, fluoranthene, pyrene and benzo(e)pyrene, none were detected in oysters. This could be due to several reasons: (a) the compounds may not have been biologically available to the oysters, (b) the oysters may have depurated them rapidly, (c) the oysters may have metabolized them to compounds which were not identified.

From this study it appears that oysters were not as useful as sediments to monitor the Bay for pollutants. This does not mean that with further refinements in methods or for special cases, where selected groups of compounds are sought, that this situation would remain.

REFERENCES

Grimmer, G. and H. Bohnke. 1972. Determination of polycyclic aromatic hydrocarbons in atmospheric dust and automotive exhaust gas by capillary gas chromatography. Fresenius Z. Anal. Chem. 261, 310-314.

Grimmer, G., K. W. Naujack and D. Schneider. 1979. Changes in PAH-profiles in different areas of a city during the year. Polynuclear aromatic hydrocarbons: chemistry and biological effects. A. Bjorseth and A. T. Dennis, Eds., Battelle Press, Columbus, Ohio, 107-125.

Lao, R. C., R. S. Thomas and T. L. Monkman. 1975. Computerized gas chromatographic-mass spectrometric analysis of polycyclic aromatic hydrocarbons in environmental samples. J. Chromatogr., 112, 681-720.

Lee, M. L., G. P. Prado, T. B. Howard and R. A. Hites. Source identification of urban airborne polycyclic aromatic hydrocarbons by gas chromatographic mass spectrometry and high resolution mass spectrometry. Biomed. Mass Spectr., 4, 182-186.

Oak Ridge Nat'l Laboratory. 1979. Identification and quantification of polynuclear organic matter (POM) on particulates from a coal-fired power plant. EPRI EA-1092, Project 1057-1.

Youngblood, W. W. and M. Blumer. 1975. Polycyclic aromatic hydrocarbons in the environment: homologous series in soil and recent marine sediments. Geochim. et Cosmochim Acta, 19, 1303-1314.

ABSTRACT

This report contains three parts. In Part I, the methodology to extract and analyze sediment and oyster tissue samples from the Chesapeake Bay is described in detail. Remaining problems are clearly identified. Part II contains the results and their discussion. Part III contains a number of appendices with detailed data. For those readers interested in still more detail, the complete bank of processed data is on computer tapes at this institute and at the Environmental Protection Agency-Chesapeake Bay Program office at Annapolis, Maryland. Also included in Part III are the results of volatile halogenated organic compounds, determined in water collected near the outfalls of several chlorine using facilities, as well as from river mouths. The distribution of the total and a few specific organic compounds within the Bay is presented by bar graphs. Mass spectrometric analyses clearly reveal the fact that one specific class of organic compounds, hydrocarbons, are the most prominent pollutants in the Bay. The application of two different search routines, one concentrating on compounds at levels > 50 ppb and the other on temporal changes, allows a quick determination of areas where problems may exist and where additional research may be indicated. Two unusual sediment samples collected during the fall 1979 cruise are discussed separately: Sample 2-19-S which clearly indicates a recent dumping of DDT and polychlorinated biphenyls, and Sample 2-27-S which contains very high concentrations of unsubstituted polynuclear aromatics.

TABLE OF CONTENTS

Page

Executive Summary iii

Abstract xxiii

Table of Contents xxiv

List of Figures xxvi

List of Tables xxviii

Acknowledgements xxx

Introduction 1

PART I 2

- 1. Sample Collection 3
- 2. Sample Preparation 14
- 3. Extraction Method and Choice of Solvent 15
- 4. Gel Permeation Chromatography 27
- 5. High Performance Liquid Chromatography 34
- 6. Gas Chromatographic Analysis 38
- 7. Gas Chromatography-Mass Spectrometry 42
- 8. Use of Computer Systems for Data Reduction and Display 45

PART II 54

- Results 55
  - Procedure Blanks 56
  - Variability of Major Organic Pollutants in Sediment Samples . . . 62
  - Problems Associated with Insufficient Resolution and Specific Detector Response 64

TABLE OF CONTENTS, continued

Page

Sediment Samples 73
Special Cases, Station 2-19-S 113
Special Cases, Station 2-27-S 120
Oyster Samples 127
Flag Tables (Specific Searches) 141
Concluding Remarks 151
References 153

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(6-70)

LIST OF FIGURES

Figure | Page

1 Chesapeake Bay sediment sample locations 4

2 Chesapeake Bay biota sample locations 5

3 Chromatograms of extracts after gel permeation chromatography:

  a. Aliquot of sediment sample extracted with diethyl ether 17

  b. Aliquot of same sample extracted with methylene chloride 18

  c. Aliquot of oyster sample extracted with diethyl ether 19

  d. Aliquot of oyster sample extracted with methylene 20

4 Mass chromatograms of fragments with $^m/_e$ = 91 in diethyl ether extracts:

  a. Sediment sample 22

  b. Oyster sample 23

5 High performance liquid chromatography-NH_2 column 37

6 Analytical scheme 44

7 Flow diagram for use of computer programs 47

8 Computer-generated displays of results:

  a. Gas chromatogram reconstructed from digitial data stored on disc 50

  b. Bar graph of the same data set 51

9 Blank chromatogram, electron capture detector 57

10 Blank chromatogram, flame ionization detector 58

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

LIST OF FIGURES, continued

Figure		Page
11-13	Mass spectra of compounds a, b, and c	59-61
14a	Demonstration of integration problems for insufficiently resolved peaks, forced baseline	65
14b	Demonstration of integration problems for insufficiently resolved peaks, vertical splitting	66
14c	Demonstration of integration problems for insufficiently resolved peaks, vertical splitting and improved baseline approximation	67
15	Mass spectrum of a peak identified in a computer search of the EC files as p,p'DDT	71
16	Mass spectrum of p,p'-DDT in sample 2-19-S	72
17-28	Station histograms for sediment samples collected during spring (a) or fall (b)	74-97
28a	Totals normalized to silt/clay	110
28b	ARI: Totals normalized to silt/clay	111
29	Location of additional sampling sites near station 19-S (June 2, 1980)	117
30	Location of additional sampling sites near station 27-S (June 2, 1980)	124
31	Susquehanna River discharge	125
32-35	Station histograms for samples of oyster tissue collected during spring (a) and fall (b)	128-136

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

LIST OF TABLES

Table		Page
1	Locations of sediment collections	6
2	Locations of oyster collections	8
3	Sediment stations, spring 1979	9
4	Oyster samples, spring 1979	10
5	Sediment stations, fall 1979	11
6	Oyster samples, fall 1979	12
7	Internal standard recoveries (CH_2Cl_2 as extraction solvent)	21
8	Recovery of aromatic standards after 48 h. contact with different solvents	26
9	Composition of standard S9 used to check extraction yields	29
10	Data for gel permeation chromatography	30
11	Gel permeation chromatography of standard compounds	31
12	HPLC fractionation of standard compounds using the elution scheme of Figure 5	35
13	Composition of the daily standard used for GC	39
14	Aromatic retention standard	40
15	Aromatic retention index	48
16	Computer-generated output from GC-MS raw data	53
17	05S-Replicates. Reproducibility of major identified peaks	63
18	Search for p,p'-DDT in E.C. data files	69
19	Search for p,p'-DDT in FID data files	70
20	Compounds identified by mass spectrometry - sediment samples	98

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER

LIST OF TABLES, continued

Table Page

21 Sediment analysis 109

22 Compounds identified in sample 2-19-S 114

23 Data on additional samples collected near station 19-S 118

24 G31, G32, G33 HPLC fraction of sample MC 1AS 119

25 Quantitation of aromatic compounds extracted from sediments near Susquehanna River mouth 121

26 Compounds identified by mass spectrometry - oyster samples . . . 137

27a List of compounds >50 ppb (dry weight) in sediment samples, spring 1979 142

27b List of compounds >50 ppb (dry weight) in sediment samples, fall 1979 144

28a List of compounds >50 ppb (dry weight) in identified oyster samples, spring 1979 148

28b List of compounds >50 ppb (dry weight) in identified oyster samples, fall 1979 149

ACKNOWLEDGMENTS

We are grateful to Dr. M. K. Cueman for his assistance with early phases of software development and mass spectrometry. C. Hein contributed in an important way to the development of software for mass spectrometric data and together with G. Wattayakorn did much of the mass spectrometric analyses. D. Bowles and S. Sturm provided us with excellent glass capillary columns. A. Chang and M. H. Chang did much of the GC work, and W. Wisher and D. Hunt helped E. Harvey keep our instruments at peak performance in the extraction laboratory. Dr. G. Ho assisted in the analyses of volatiles. Thanks are also due to H. Slone for his supervision of the GC and extraction laboratory. It was a pleasure to have the non-tiring assistance of S. Swete and S. Presson for the typing. Finally, we are indebted to the Chesapeake Bay Program of the Environmental Protection Agency for giving us the opportunity to work on these challenging problems.

9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA. OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS.
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

INTRODUCTION

The production of synthetic organic chemicals has greatly increased since the Second World War. The benefits from these are obvious: pesticides to insure better crop yields, synthetic fibers with a variety of properties which sometimes make them more desirable than natural ones, and plastics of all sorts to replace glass and metals in a variety of uses. The list could go on and on. Unfortunately, there are times when the benefits are outweighed by environmental costs. These costs are incurred when toxic synthetic organics enter the environment due to misuse, ignorance in assessing their total impact, careless discharges or spills. When they enter the natural environment, these chemicals may be taken up by plants and animals from where they may accumulate in food chains. This can lead to toxic effects (acute or chronic) in plants and animals or the substance can accumulate to levels in animals that makes them unfit for human consumption. Either way, the environmental costs are high.

Research reported in this document is the result of a project designed to develop reliable information on organic compounds in the Chesapeake Bay which have previously been designated toxic as well as those which have not been categorized as either toxic or non-toxic due to lack of study.

Before this objective could be reached, several obstacles had to be overcome and decisions had to be made. These included:

(a) The selection of sample types
(b) The selection of sampling locations
(c) The method of sample preparation
(d) The method of sample extraction
(e) The method of fractionating the extract
(f) The methods of compound identification and quantification

The selections and decisions would have been greatly simplified if a pre-determined group of compounds to be looked for had been chosen. However, limiting the search to such a group would obviously eliminate the likelihood of finding compounds not in this group. Therefore, we attempted to develop an analytical scheme which would extract, identify and quantitate as broad a spectrum of organic compounds as possible with gas chromatography and gas chromatography-mass spectrometry. This, of course, limits the set to those which are stable and volatile enough to pass through a gas chromatograph. Also, it must be realized that any extraction scheme which is intended to yield a broad spectrum of compounds will likely sacrifice some quantitative information for more qualitative data.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER
EPA-287 (Cin)
(4-76)

PART I

1. SAMPLE COLLECTION

The number of samples that can be analyzed for their content of organic componds is limited because of the effort involved in such analyses. For this reason, it is not feasible to lay down a grid and mechanically collect sediment samples at every node. As an alternative, the locations were selected according to their potential to contain pollutants, their representation of a particular area of the Bay (upper, central, lower) and their closeness to existing oyster beds from which the tissue samples had to be taken.

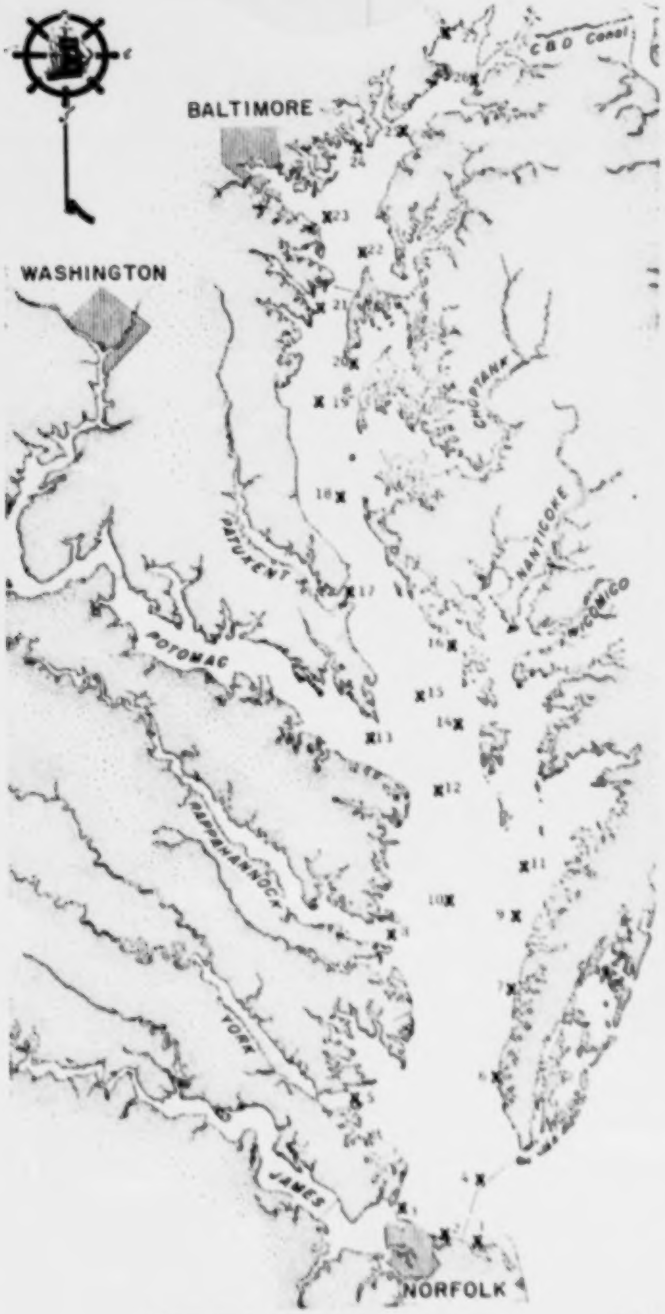
Sediment and oyster sampling locations are shown in Figures 1 and 2. The locations of these sampling areas are described in Tables 1 and 2. Position data were determined by Loran C and by shore bearings that were translated on charts to latitude and longitude. Both sets of data are given in Table 3 and Table 4 for the first cruise, and in Table 5 and Table 6 for the second cruise.

During the first sediment collection cruise, Loran C reception was poor for stations north of 19, leading to questionable accuracy for the Loran C coordinates. In such cases, station reoccupation was based on shore bearings. A more sophisticated Loran C system was used during the second cruise and accurate bearings were obtained for all stations.

Loran C was not available for much of the first oyster collection cruise. Station reoccupation was thus based on shore bearings, but Loran C coordinates again were obtained in the second cruise.

Using the two strongest Loran C chains only for reporting, the position accuracy was estimated to be within 200 ft. A comparison with shore bearings in some cases, however, indicated that the accuracy was much better. The conversion of Loran C coordinates to latitude-longitude coordinates is not always accurate (even though Loran C coordinates may be very reproducible) due to differences in wave propagation over land and water. Proper correction factors to account for these effects are not yet available for the Chesapeake Bay. Thus, where latitude and longitude coordinates have been derived from Loran C data, the latter are more accurate.

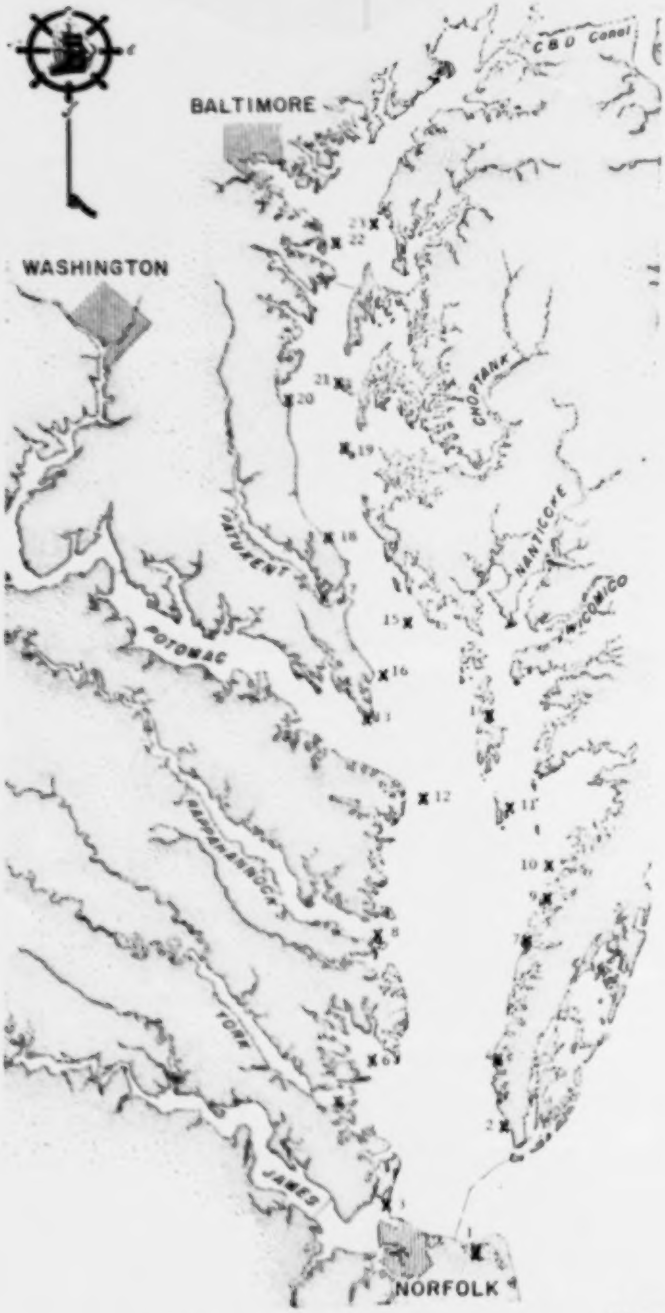
All sediment samples were collected with a 0.1 m^2 stainless steel Smith-McIntyre grab sampler (manufactured by the University of Rhode Island, School of Oceanography). Precautions to prevent contamination included rinsing with sea water (from an intake 4 ft. below the surface) and methanol. During sample retrieval, the integrity of the collected sediments was protected by solid stainless steel doors covering the top of the sample. Of the contained sediment, only the top 3 cm were transferred


BALTIMORE
WASHINGTON
NORFOLK
C & D Canal
CHOPTANK
NANTICOKE
WICOMICO
PATUXENT
POTOMAC
RAPPAHANNOCK
YORK
JAMES
26
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
1

Chesapeake Bay Sediment Sample Locations

Figure 1

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)


BALTIMORE
WASHINGTON
NORFOLK
C&D Canal
CHOPTANK
NANTICOKE
WICOMICO
PATUXENT
POTOMAC
RAPPAHANNOCK
YORK
JAMES
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

Chesapeake Bay Biota Sample Locations

Figure 2

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 1

Locations of Sediment Collections

1. Lynnhaven Inlet mouth, an area of intense small boat traffic.
2. Little Creek Inlet mouth, a Naval Base with considerable ship traffic and maintenance activities.
3. Channel leading to Hampton Roads, positioned to demonstrate inputs from commercial activity in the James and Elizabeth Rivers.
4. Bay mouth, north channel, representative of this region.
5. York River mouth, with inputs from paper and oil industries as well as Naval traffic.
6. Cherrystone Inlet mouth, potential agricultural chemical runoff.
7. Nassawodax Creek mouth, potential agricultural chemical runoff.
8. Rappahannock River mouth, the major river input in the area.
9. Nandua Creek mouth, potential agricultural chemical runoff.
10. Midbay transect.
11. Junction of Pocamoke and Tangier Sounds representing potential agricultural chemical runoff.
12. Midbay transect.
13. Potomac River mouth, monitoring inputs from many types of commercial activities.
14. Northwest of Smith Island, potential agricultural chemical runoff from Wicomico River area.
15. Midbay transect.
16. Hooper Straits, potential agricultural chemical runoff from Nanticoke River area.
17. Patuxent River mouth,monitoring inputs from military and industrial establishments.
18. Midbay transect.

Table 1 (continued).

Locations of Sediment Collections
-2-

19. Midbay transect.
20. Eastern Bay mouth, potential agricultural chemical runoff.
21. Severn River mouth, covering urban runoff from the Annapolis area.
22. Northern tip of Kent Island, potential agricultural chemical runoff.
23. Baltimore Harbor mouth, monitoring a multitude of potential pollution sources.
24. Gunpowder River mouth with urban, industrial and military inputs.
25. Midbay transect.
26. Elk River mouth, potential agricultural chemical runoff, representing inputs through C & D canal.
27. Susquehanna River mouth, covering the major river input to Chesapeake Bay with its industrial runoff.

TABLE 2

LOCATIONS OF OYSTER COLLECTIONS

1. Lynnhaven Inlet
2. Kiptopeke Inlet
3. Hampton Roads Bridge Tunnel
4. North side of Cherrystone Inlet
5. York River - 0.25 mi from oil refinery
6. Middle of Mobjack Bay
7. Mouth of Occohannock Creek
8. Rappahannock River mouth
9. Hacks Neck on south side of Butcher Creek
10. Outside Onancock Inlet
11. 0.25 mi east of Tangier Island
12. 1.5 mi southwest of Smith Point light
13. Potomac River mouth
14. Kedges straight north of Smith Island
15. 10 meters north of Hooper Is. light
16. 15 meters north of Point No Point light
17. Patuxent River mouth
18. 0.25 mile off Calvert Cliffs nuclear power plant
19. 300 meters north of Sharp Island light
20. 500 meters north of Holland Point
21. 1 mile west of Poplar Island
22. Belvedere Shoal along Baltimore entrance channel
23. 2 miles southwest of Swan Point

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER

TABLE 3

SEDIMENT STATIONS SPRING 1979

STATION #	LORAN COORDINATES		LATITUDE	LONGITUDE
01S	27194.6	41255.7	36° 55.2'	76° 05.3'
02S	27218.1	41258.4	36° 56.3'	76° 10.7'
03S	27250.2	41291.9	37° 00.0'	76° 17.0'
04S	27210.7	41353.8	37° 03.5'	76° 05.3'
05S	27204.5	41453.9	37° 14.6'	76° 23.1'
06S	27225.1	41515.9	37° 17.2'	76° 02.7'
07S	27231.9	41653.7	37° 28.2'	75° 58.5'
08S	27328.5	41709.9	37° 35.4'	76° 17.7'
09S	27253.7	41767.3	37° 38.1'	75° 58.8'
10S	27298.9	41768.0	37° 39.3'	76' 08.9'
11S	27253.6	41844.5	37° 44.2'	75° 55.8'
12S	27333.0	41928.7	37° 52.9'	76° 09.2'
13S	27403.5	42011.4	38° 00.9'	76° 20.7'
14S	27345.5	42039.6	38° 01.9'	76° 07.0'
15S	27382.1	42084.1	38° 06.3'	76° 12.7'
16S	27373.6	42766.4	38° 12.6'	76° 07.1'
17S	27466.8	42233.1	38° 19.5'	76° 23.5'
18S	27504.7	42385.8	38° 32.2'	76° 24.9'
19S	27556.5	42538.4	38° 45.1'	76° 26.4'
20S			38° 49.8'	76° 20.8'
21S			38° 56.9'	76° 25.9'
22S			39° 04.8'	76° 19.1'
23S			39° 10.5'	76° 27.2'
24S			39° 18.2'	76° 18.9'
25S	27605.6	42975.8	39° 20.3'	76° 11.6'
26S	27566.9	43056.4	39° 26.3'	76° 00.3'
27S	27612.2	43129.3	39° 32.5'	76° 04.5'

EPA-287 (Cin.)
(4-76)

TABLE 4

OYSTER SAMPLES SPRING 1979

STATION #	LORAN COORDINATES		LATITUDE	LONGITUDE	UNCERTAINTY
01B			36° 53.3'	76° 4.6'	± 0.3 mi
02B			37° 10.0'	75° 59.3'	
03B			37° 00.4'	76° 19.3'	
04B			37° 18.3'	76° 01.0'	
05B	27313.0	41438.4	37° 13.7'	76° 25.6'	± 0.1 mi
06B	27303.4	41507.9	37° 18.8'	76° 20.7'	± 0.1 mi
07B			37° 33.6'	75° 56.0'	
08B	27332.9	41699.6	37° 34.8'	76° 19.2'	
09B			37° 39.1'	76° 52.6'	
10B	27233.8	41847.7	37° 44.0'	75° 51.5'	
11B	27276.0	41912.5	37° 50.3'	75° 57.7'	
12B	27342.0	41911.9	37° 51.8'	76° 12.0'	± 0.2 mi
13B			38° 02.7'	76° 20.0'	± 0.1 mi
14B			38° 02.9'	76° 01.0'	± 0.2 mi
15B			38° 15.4'	76° 15.0'	
16B			38° 07.9'	76° 17.4'	
17B			38° 19.0'	76° 27.2'	± 0.1 mi
18B			38° 25.9'	76° 25.7'	± 0.2 mi
19B			38° 38.4'	76° 22.6'	
20B			38° 44.0'	76° 31.7'	± 0.2 mi
21B			38° 46.2'	76° 23.6'	± 0.1 mi
22B			39° 05.7'	76° 22.9'	± 0.1 mi
23B			39° 07.3'	76° 17.2'	

Navigation was by LORAN C, when available, and by shore bearings. The uncertainty in position is much larger than in sediment sampling, reflecting the natural difficulties in collecting any marine biota. This uncertainty represents the distance the vessel moved in collecting the samples at a particular station. Where no uncertainty is reported, the sample was collected at the given position as nearly as could be determined by navigation methods available.

TABLE 5

SEDIMENT STATIONS FALL 1979

STATION #	LORAN COORDINATES		LATITUDE	LONGITUDE
01S	27194.6	41255.7	36° 55.2'	76° 05.3'
02S	27218.0	41258.4	36° 55.2'	76° 10.8'
03S	27250.2	41291.9	37° 00.0'	76° 17.0'
04S	27210.7	41353.8	37° 03.5'	76° 05.3'
05S	27304.5	41453.9	37° 14.6'	76° 23.1'
06S	27225.2	41516.0	37° 17.1'	76° 02.8'
07S	27231.9	41653.7	37° 28.2'	75° 58.5'
08S	27328.5	41709.9	37° 35.5'	76° 17.7'
09S	27253.7	41767.3	37° 38.1'	75° 58.8'
10S	27298.9	41768.0	37° 39.3'	76° 08.9'
11S	27253.6	41844.6	37° 44.3'	75° 55.8'
12S	27333.0	41928.7	37° 52.9'	76° 09.2'
13S	27403.5	42011.4	38° 1.0'	76° 20.7'
14S	27345.5	42039.6	38° 01.9'	76° 07.0'
15S	27382.1	42084.1	38° 06.2'	76° 12.7'
16S	27373.6	42166.4	38° 12.6'	76° 07.1'
17S	27466.8	42233.1	38° 19.5'	76° 23.5'
18S	27504.6	42385.8	38° 32.2'	76° 24.9'
19S	27556.5	42538.4	38° 45.1'	76° 26.4'
20S	27545.8	42600.4	38° 49.8'	76° 20.8'
21S	27592.5	42682.5	38° 56.9'	76° 25.7'
22S	27587.3	42784.7	39° 4.8'	76° 19.3'
23S	27625.4	42836.8	39° 09.4'	76° 23.7'
24S	27635.5	42948.8	39° 18.3'	76° 19.2'
25S	27605.6	42975.8	39° 20.2'	76° 11.8'
26S	27566.8	43056.6	39° 26.4'	76° 59.9'
27S	27612.2	43129.3	39° 32.6'	76° 04.2'

BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER
EPA-287 (Cin.)
(4-75)

TABLE 6

OYSTER SAMPLES FALL 1979

STATION #	LORAN COORDINATES		LATITUDE	LONGITUDE	UNCERTAINTY
01B			36° 53.3'	76° 04.6'	± 0.3 mi
02B			37° 10.0'	75° 59.3'	
03B			37° 00.4'	76° 19.3'	
04B			37° 18.3'	76° 01.0'	
05B	27313.0	41438.0	37° 13.6'	76° 25.7'	
06B	27304.8	41502.4	37° 18.5'	76° 21.1'	± 0.1 mi
07B			37° 33.6'	75° 56.0'	
08B	27333.1	41701.4	37° 34.9'	76° 19.1'	
09B			37° 39.1'	76° 52.6'	
10B	27234.0	41847.9	37° 44.1'	76° 51.5'	
11B	27276.0	41912.0	37° 50.3'	75° 57.0'	
12B	27341.1	41926.3	37° 52.8'	76° 11.1'	
13B	27405.6	42036.5	38° 03.0'	76° 20.0'	
14B	27314.6	42059.5	38° 02.9'	75° 59.7'	± 0.2 mi
15B	27416.5	42192.0	38° 15.4'	76° 15.0'	
16B	27407.1	42097.5	38° 07.8'	76° 17.5'	
17B	27474.0	42225.1	38° 19.1'	76° 25.5'	± 0.2 mi
18B	27494.4	42308.5	38° 26.0'	76° 25.7'	
19B	27518.0	42463.2	38° 38.5'	76° 22.6'	
20B	27574.0	42529.3	38° 44.6'	76° 30.6'	
21B	27548.1	42550.2	38° 45.8'	76° 24.1'	± 0.2 mi
22B	27610.0	42798 8	39° 06.2'	76° 22.8'	± 0.2 mi
23B	27595.2	42831.5	39° 8.6'	76° 18.0'	

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
7/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

to precleaned one-quart glass jars (detergent washed, acetone rinsed and heated to 200°C for 12 hours), using a methanol rinsed stainless steel scoop. The jars were sealed tight with Teflon-lined covers and immediately placed in a box containing dry ice, where they remained until freeze drying.

Most oysters were collected with a four-foot wide commercial oyster dredge, with the exception of stations 1, 2, 3, 4, 7 and 9. At station 1, there are no public oyster grounds and the oysters had to be bought from the owner of the beds. At station 2, the oysters were scraped from concrete pilings at the Kiptopeke ferry pier. At station 3, they were scraped from the concrete pilings at the northern span of the Hampton Roads Bridge Tunnel (at a depth of 2 ft. below surface). At stations 4, 7 and 9, the oysters were taken by hand from shallow tidal mud flats.

All oysters were kept alive on ice until shucking, which was done on shipboard when conditions permitted. Otherwise they were shucked in the laboratory within 12 hours from collection. In both cases, the oyster shells were cleaned under flowing water with a wire brush before they were opened. Liquor and meats were transferred to precleaned glass jars, sealed with Teflon-lined covers and stored on dry ice until freeze drying.

2. SAMPLE PREPARATION

Frozen sediment samples were thawed at room temperature and transfered to clean stainless steel trays for freeze drying. In order to prevent contamination of samples during the freeze-drying process, it was found necessary to periodically clean the chamber walls with solvents and subsequently run the freeze dryer for approximately two days at elevated temperatures (100°C). In addition, the sample trays are shielded by covering them loosely with solvent rinsed aluminum foil. A stream of clean N_2 was fed into the vacuum line to prevent backstreaming of pump oil. The pressure in the line was held at 250 microns. Clean N_2 was again used to bring the drying chamber up to atmospheric pressure at the end of the freeze-drying process. Freeze drying of sediments takes approximately 48 hours. Homogenization was effected after the freeze-drying process in a stainless steel pan with cover. Eight steel balls of 2 cm diameter and mechanical agitation was used to break up and homogenize the sediment. The resulting dry, fine powder was transferred to Teflon-covered jars and kept in a freezer at approximately -25°C until extraction.

Oysters were allowed to thaw at room temperature, homogenized at 45,000 rpm in a Virtis homogenizer (Model #45) and then transferred into stainless steel trays. Freeze drying of oysters takes approximately 36 hours. The dry cake was broken up into small pieces with a mortar and pestle, transferred into a glass vial and stored in a freezer until extraction.

3. EXTRACTION METHOD AND CHOICE OF SOLVENTS

Compared to pure hydrocarbons, organic compounds possessing functional groups or heteroatoms within ring structures can be expected to be more prone to modification by chemical reactions. For environmental samples, which commonly contain large numbers of organic compounds, a multiplicity of artifacts is likely to result from methodology that is not carefully executed. Thus, much attention and careful screeing of extraction methods are indicated.

Two main parameters are available to prevent the generation of artifacts: the solvent and the method of extraction. Their choice, however, also depends on extraction yields. Very little is known about the detailed mechanisms involved in the extraction of organic compounds from sediment and tissue. While the extraction of such compounds in tissue probably is influenced mainly by simple partitioning, there is always some doubt that the solvent makes effective contact to allow partitioning to take place (this would require breaking of all cell walls). In sediments, the interplay between mineral matrices and organic material is so complex (and dependent on sediment type) that any attempt to hypothesize about mechanisms of extraction seems pointless. Thus, an empirical approach is likely to provide the best answers.

Five solvents were selected to check the extraction yields and to evaluate artifact formation in both sample types. These were:

(a) Diethyl ether (Et_2O)
(b) Methylene chloride (CH_2Cl_2)
(c) Tetrahydrofuran (THF)
(d) Ethyl acetate (EtAc)
(e) Methanol-toluene azeotrope

Soxhlet apparatus was chosen as the physical method of extraction because it has the dual advantage of leaving the sample cool and providing an efficient, continuous reflux-distillation extraction. Extraction methods that expend more energy in the sample (reflux extraction, ultrasonic agitation) were discarded because of the potential for artifact generation.

Two of the solvents, THF and EtAc, were quickly eliminated because of impurities present. The methanol-toluene azeotrope led to the formation of artifacts (methyl-esters) that interfered with the analysis at a later stage. Et_2O and CH_2Cl_2 both appeared to give similar extraction yields as judged from internal standards and comparison of chromatograms. Both solvents were similar in their extractive power based on recovery of added internal standards, but extracts with Et_2O appeared to be more complex

Figures 3A to 3D). Recoveries for CH_2Cl_2 at two different spiking levels are presented in Table 7.

In a next step, these differences were further pursued in ten replicate extracts of sediment and oyster tissue. Without addition of a multiple-compound internal standard, chromatograms of extracts from the two sample types with both solvents indicated substantial compositional differences, while the replicates within one sample type and one solvent were very uniform. An inspection of mass spectra from GC-MS runs provided additional evidence for compositional differences and at the same time furnished some clues about their origin. Most of the major components in Et_2O extracts had mass spectra that were dominated by a tropylium ion ($m/e = 91$), (Figure 4), with little additional fragmentation that could positively be identified as originating from one compound. Other characteristic mass spectra found only in Et_2O extracts contained fragment pairs at $m/e = 45$ and 73. Both sediment and tissue extracts had one compound in common which was identified as bibenzyl (1,2-diphenylethane). Many more mass spectra of similar characteristics were present in Et_2O extracts of both sample types, but they were not identical. Further evidence for this fact emerged from retention information which, again with the exception of bibenzyl, differed between sediment extracts and tissue extracts. None of these compounds were found in extracts with CH_2Cl_2, although an active search was made for them. An estimate of the ratio of the mass spectrometric detection limit to the signals encountered for these compounds in Et_2O extracts ($<1/10^2$) made it unlikely that these compositional differences were caused by differences in extraction yields. Thus, our efforts focused on artifacts, and the following hypothesis was adopted to further test the generation of artifacts in Et_2O extracts. Since both sample types have a common denominator in bibenzyl and the mass spectra of a large number of compounds in Et_2O extracts were bibenzyl-like, this compound was a prime suspect. It is known that under proper circumstances, bibenzyl can react to form (very stable) benzyl-type radicals. Trace amounts of peroxide in Et_2O could provide such a reaction mechanism via hydroperoxide radicals (Meislich et al., 1977; Merck Index 1976). The benzyl radicals could then react with components of the sample to generate artifacts that were different for both sample types.

The basic correctness of these observations was confirmed on a sediment collected in a different area of the Bay. A decision to proceed with CH_2Cl_2 at this point would seem to be indicated, except for the fact that problems were encountered earlier with this solvent. Although nothing unusual could be detected by GC-MS in CH_2Cl_2 extracts, E.C.-chromatograms indicated the formation of low level chlorinated artifacts or contaminants. It was established by experiment that artifact formation or contamination occurs during the reflux phase in the Soxhlet apparatus, and that the presence or absence of a thimble is of no consequence. Maximum concentration of individual artifacts or contaminants were estimated to be at levels <10 ppb. Since the detection of chlorinated compounds in the Bay environment is of major importance and the origin of these artifacts is not understood, the use of CH_2Cl_2 cetainly is not ideal. Thus, it was decided to further pursue the problems encountered with Et_2O and try to eliminate

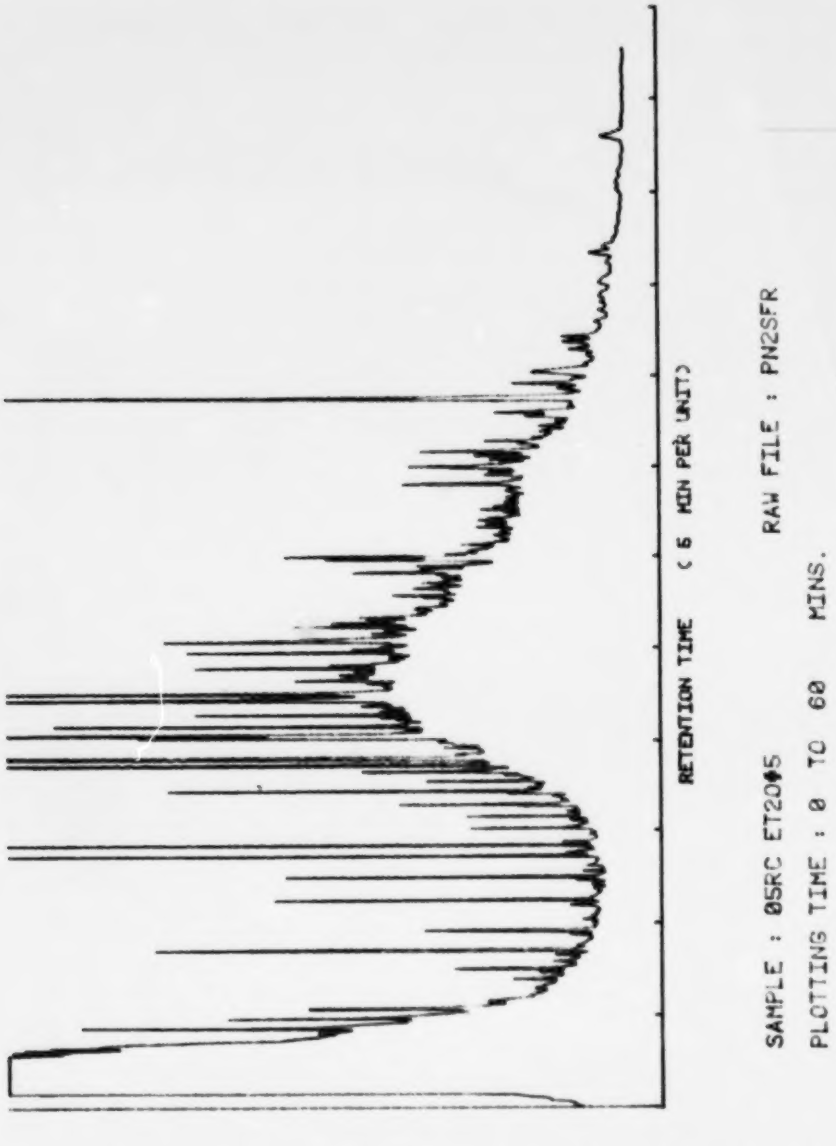


Figure 3a. Gas chromatogram of extracts after gel permeation chromatography. Aliquot of sediment sample extracted with diethyl ether.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-78)

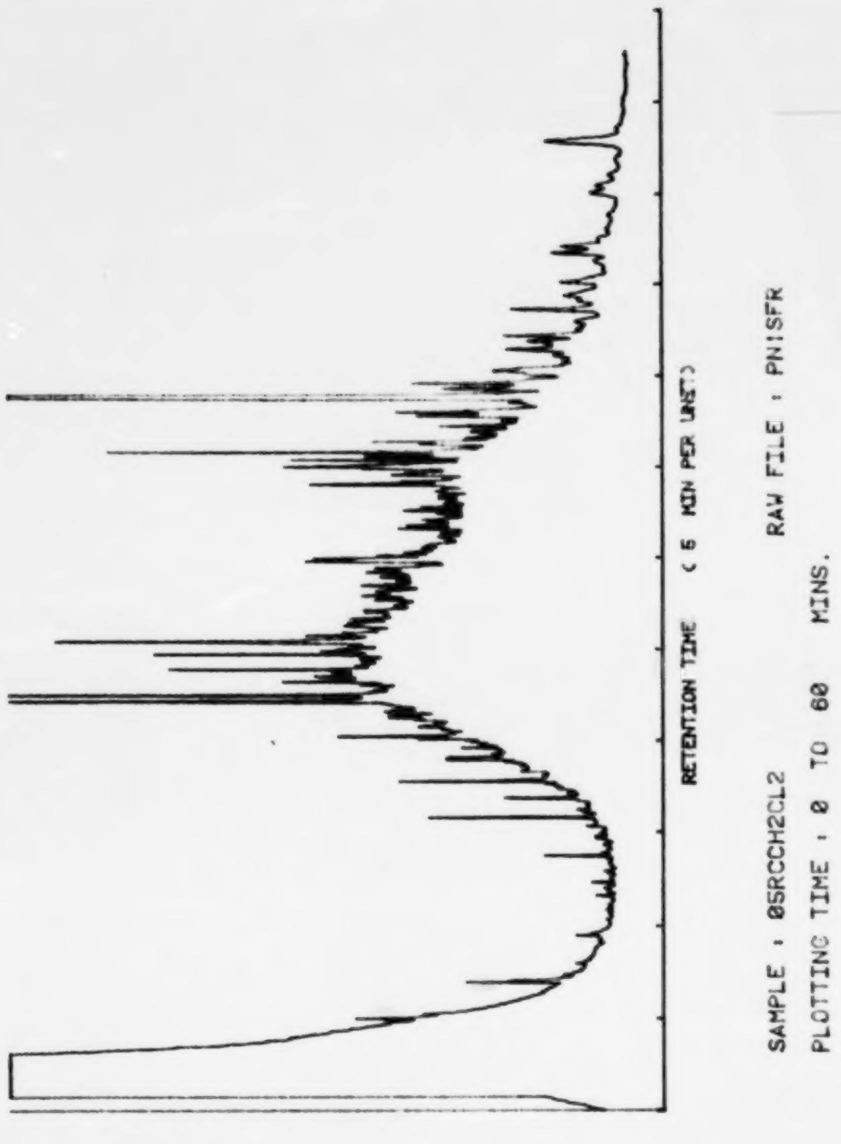


Figure 3b. Gas chromatogram of extracts after gel permeation chromatography. Aliquot of same sample extracted with methylene chloride.

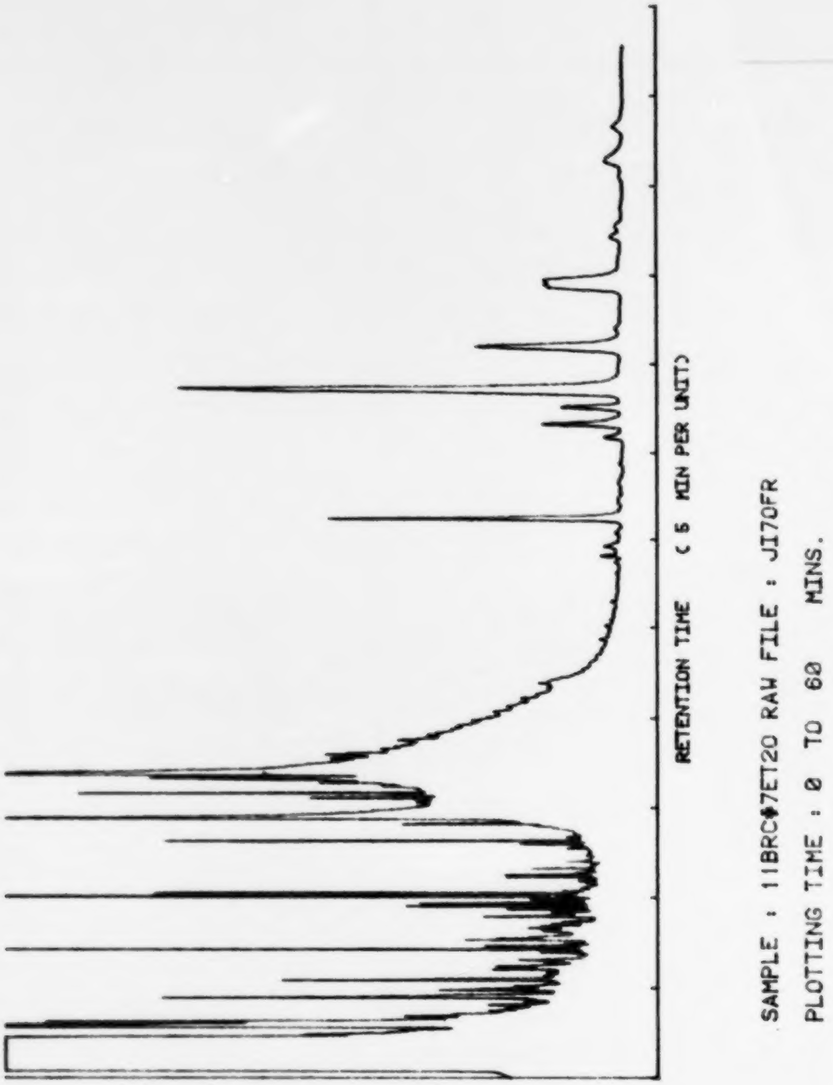


Figure 3c. Gas chromatogram of extracts after gel permeation chromatography. Aliquot of oyster sample extracted with diethyl ether.

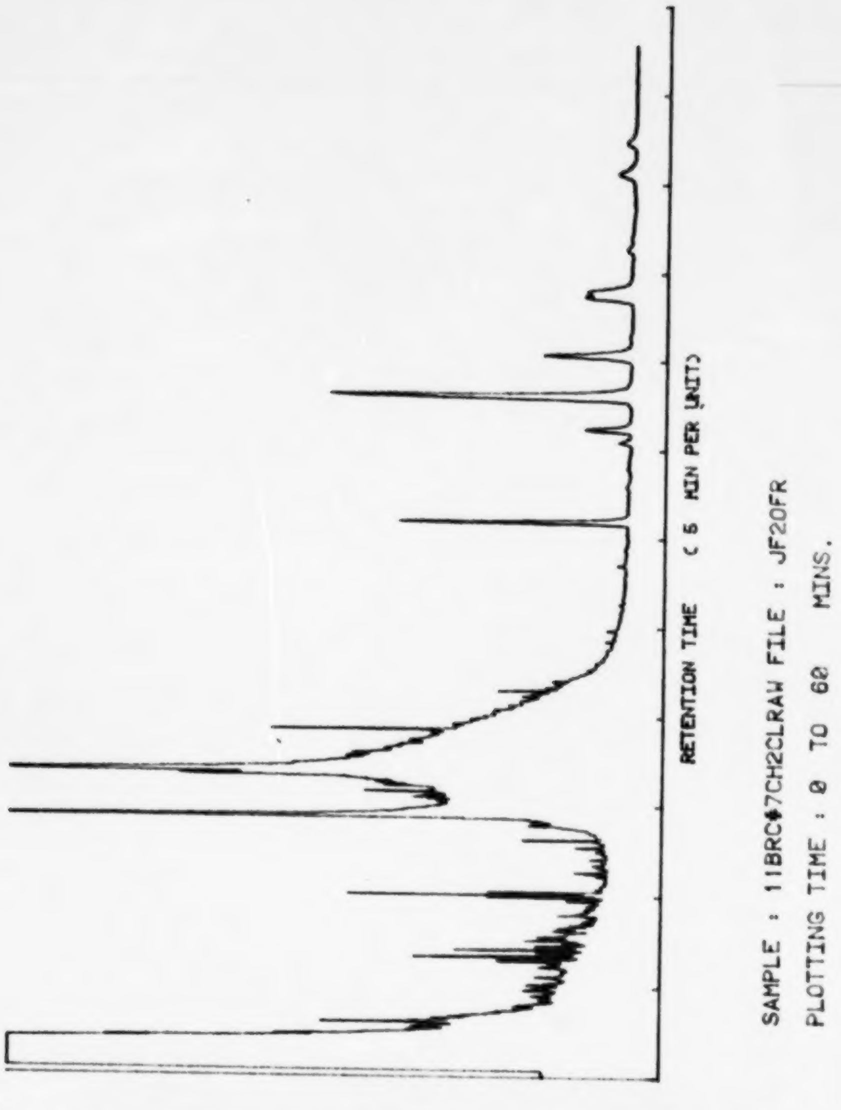


Figure 3d. Gas chromatogram of extracts after gel permeation chromatography. Aliquot of same sample extracted with methylene chloride.

EPA-287 (Cin.)
(4-76)

Table 7: Internal Standard Recoveries (CH_2Cl_2 as Extraction Solvent)

At the lower spiking level, internal standards were added to exhaustively extracted and then rewetted sediment. This was followed by freeze drying. The spikes at higher levels were added directly to exhaustively extracted and dried sediment. The rest of the procedure (48-hour Soxhlet extraction, solvent evaporation and injection into GC) was the same for both samples.

Compound	Spike Level (ppb)	% Recovery, Sediment Aliquot 1	% Recovery, Sediment Aliquot 2	% Recovery, Sand
Phenyl Ether	57	17	36	
	625	59		69
Dibenzothiophene	55	43	56	
	600	62		72
Atrazine	54	56	75	
	625	73		76
Dibutyl Phthalate	71	56	60	
	725	73		84
Malathion	87	63	70	
	500	68		79
Fluoranthene	85	53	53	
	725	68		80
o,p'-DDD	2	37	38	
	18	74		84
Benzo(e)pyrene	216	58	52	
	2000	76		86
Decachlorobiphenyl	45	--	--	
	400	77		91

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER

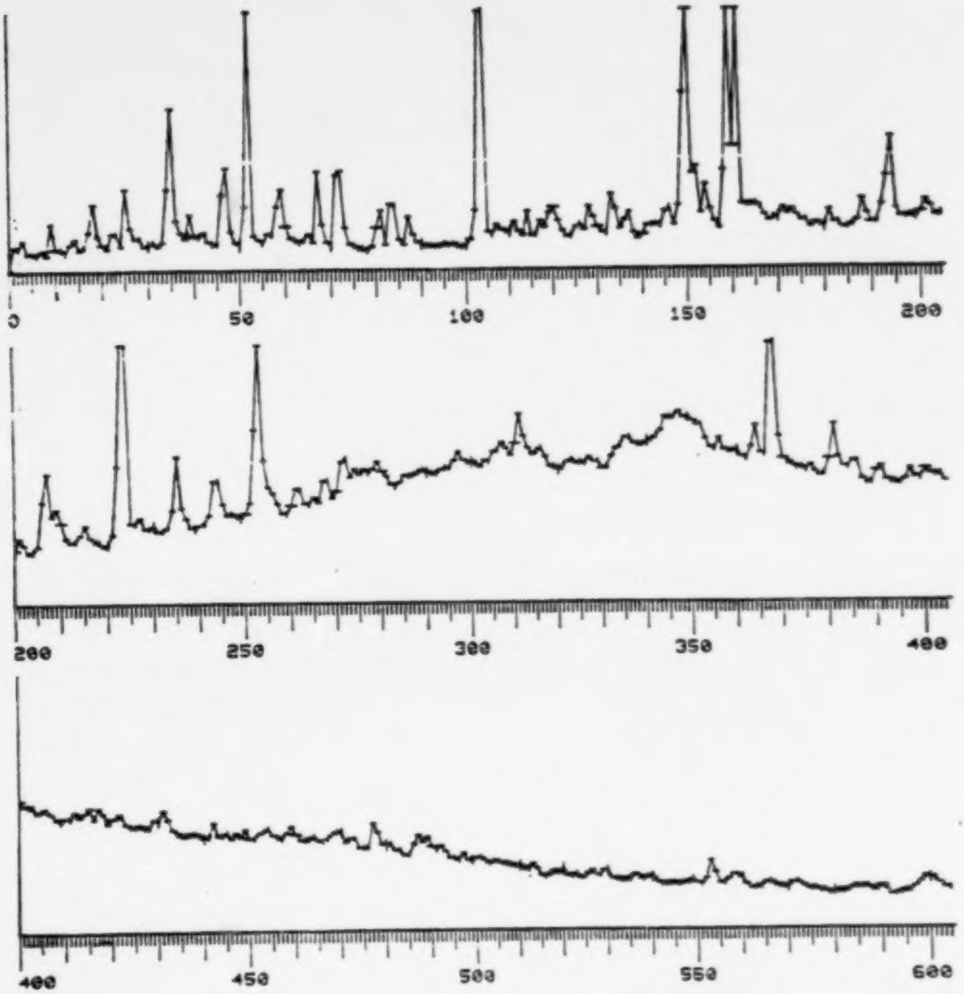


Figure 4A

Mass chromatograms of fragments with $^m/e = 91$ in diethyl ether estracts. Sediment sample.

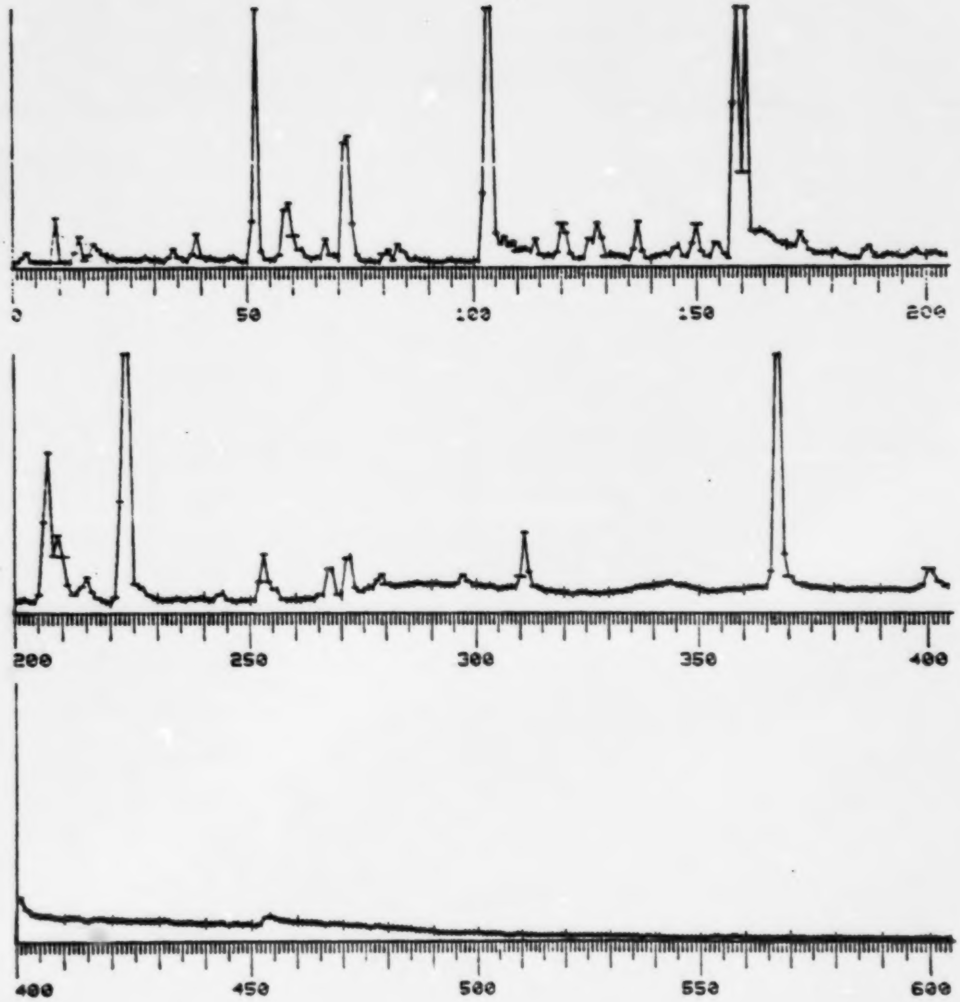


Figure 43

Mass chromatograms of fragments with $^m/e = 91$ in diethyl ether extracts. Oyster sample.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin)
(4-78)

bibenzyl or to break the chain of reactions that eventually lead to the artifacts.

Elimination of bibenzyl or purchase of bibenzyl-free Et_2O proved to be impossible. It is equally impractical to eliminate the presence of ether peroxide by distillation in a routine appication of this solvent. Thus, further experiments concentrated on checks to assure that the benzyl radical hypothesis was basically correct and to try to quench the formation of this radical. The following variations for the extraction were incorporated:

(a) Addition of synthesized bibenzyl to CH_2Cl_2

(b) Addition of synthesized bibenzyl to Et_2O to approximately double the original concentration.

(c) Addition of quinone to Et_2O to quench the benzyl radical formation

Extractions of a homogenized sediment were repeated with solvents a to c and, in addition, again with unmodified Et_2O and CH_2Cl_2. The extract with solvent a, compared with the pure CH_2Cl_2 extract, contained bibenzyl as the only extra peak in the chromatogram. The extract with solvent b qualitatively was similar to an extract with regular Et_2O, but the artifact concentrations were not increased according to expectations. Solvent c gave an extract that contained again an abundance of artifacts similar to b and contained no evidence that any quenching to suppress the bibenzyl radical occurred. In retrospect, it was concluded that the amount of quinone added to Et_2O may have been consumed mainly by the peroxide. Thus, while the results of these experiments proved that the formation of artifacts is not yet fully comprehended, they also demonstrated that there is no simple solution to a suppression of such artifacts. This left us with no other choice than CH_2Cl_2, although it is by no means beyond criticism.

The artifact problem was further pursued after all samples had been extracted with CH_2Cl_2. A series of unsubstituted PNA's were exposed for 48 hours to the following solvents:

(a) Et_2O, "distilled in glass" grade (from bottle; contains 10ppb bibenzyl)

(b) CH_2Cl_2, "distilled in glass" grade

(c) CH_2Cl_2 + residue of Et_2O from bottle after concentration in a rotary evaporator

(d) Freshly distilled Et_2O

(e) Freshly distilled Et_2O + 30ppb of bibenzyl

(f) CH_2Cl_2 + 30ppb of bibenzyl

Percent recoveries are presented in Table 8. An interpretation of these data clearly suggests that the ether peroxide is primarily responsible for the artifacts and that radical-formation is not limited solely to the presence of bibenzyl.

TABLE 8

Recovery of Aromatic Standards after 48 h. contact with different solvents.

Precision is 1 standard deviation from triplicate analysis.

Standard Compound	Et_2O from bottle	CH_2Cl_2	Et_2O Residue In CH_2Cl_2 1)	Redistilled Et_2O	Bibenzyl + Redist. Et_2O	Bibenzyl + CH_2Cl_2
Biphenyl	31.0 ± 4.4	72.5 ± 5.1	57 ± 12	40.9 ± 6.4	42.4 ± 6.0	76.4 ± 7.2
Hexamethylbenzene	46 ± 16	72.4 ± 4.3	64 ± 13	39.5 ± 6.5	42.4 ± 5.8	67.9 ± 5.1
Phenanthrene	73 ± 11	71.4 ± 2.0	60 ± 16	41.7 ± 8.4	49 ± 11	76.2 ± 0.4
Anthracene	33.0 ± 5.6	75.8 ± 4.6	7.4 ± 2.0	43.2 ± 7.5	52.2 ± 5.8	78.3 ± 0.6
Pyrene	68.0 ± 4.6	80.7 ± 6.2	45.8 ± 8.2	54 ± 10	66.2 ± 4.5	83.6 ± 4.7
Chrysene	82.9 ± 9.3	84.4 ± 4.8	69 ± 17	74.7 ± 9.2	83.2 ± 2.4	89.1 ± 4.0
Perylene	-0-	89 ± 11	-0-	39.1 ± 6.4	53.1 ± 5.1	92.7 ± 5.8
Benzo(ghi)perylene	48.9 ± 7.4	90 ± 14	4.2 ± 1.1	73.4 ± 5.5	69 ± 13	94.1 ± 10.3

---

1) Residue from redistillation of 300 ml Et_2O;(5ml) added to 250 ml CH_2Cl_2

4. GEL PERMEATION CHROMATOGRAPHY (GPC)

Any method of extraction that is designed to give reasonable extraction efficiencies for a broad spectrum of organic compounds, is likely to contain large amounts of non-toxic solutes. Thus, a major problem encountered in such extracts was the overwhelming presence of biogenic substances that completely buried any toxic organic compounds at expected levels. Based on mass spectral information, which suggested many of the major peaks in the chromatogram to be of steroid/terpenoid structure, GPC was selected as a major candidate for a first separation of these extracts.

In the choice of a suitable resin, we were guided mainly by a comprehensive survey of the elution behavior of pesticides (Pflugmacher and Ebing, 1978). Four different BioBeads, S-X2, S-X3, S-X8 and S-X12 were tried. With the exception of S-X12 (exclusion limit: M.W. 400), in which much of the toxic compound test mixture S9 (Table 9) was co-eluted with biogenic lipids, all BioBeads have similar separation abilities. However, S-X8 required the least amount of solvent and was preferred for that reason. Proper separation was further investigated with four different solvent systems: toluene/EtAc (3/1), CH_2Cl_2, n-C_6H_{14}/CH_2Cl_2 (50/50) and (85/15). Good separation of toxic compounds in S9 from biolipids was achieved by both CH_2Cl_2 and toluene/EtAc, but the latter contained too many impurities (from EtAc). n-C_6H_{14}/CH_2Cl_2 (85/15) finally led to unacceptable separation. BioBeads S-X8 and CH_2Cl_2 were thus accepted as basic column parameters for the gel permeation chromatography. Details are found in Table 10.

Further studies centered around the determination of elution volumes for toxic organic substances, to be collected for further separation on high performance liquid chromatography. While it was originally envisioned to separate three fractions (0-140 ml, containing mainly biogenic and other non-toxic compounds for disposal, 140-220 ml, containing essentially all toxic compounds of concern, and > 220 ml, containing sulfur, again for disposal), this turned out to be impossible. In a first methodology report (Bieri *et al.*, 1979a) it was mentioned that the first fraction contained at least two compounds that should be considered for anlaysis: dibutyl phthalate and malathion. More comprehensive testing revealed the presence of seven more at 100% and of eleven from aproximately 2% to 80% in this fraction. Details are found in Table 11. It is likely that still more toxic organic compounds will elute in this fraction in a sample extract, and as a consequence, this fraction as a whole cannot be discarded. Further tests suggest four fractions must be distinguished: fraction G1 from 0-100 ml, fraction G2 from 100-140 ml, fraction G3 from 140-220 ml and fraction G4 > 220 ml. Most man-made toxic organic compounds have a high probability of eluting in fractions G2 and G3, while G1 and G4 can be discarded.

In practice, a further separation or analysis of G2 turned out to be limited by technical problems. There are so many large and very polar molecules in this fraction that damage to either the HPLC column or to GC-capillary occurs after just a few samples. Thus, before G2 can be analyzed it will be necessary to remove these molecules by some additional step.

TABLE 9

COMPOSITION OF STANDARD S9 USED TO CHECK EXTRACTION YIELDS.

COMPOUND	CONCENTRATION (ng/µl)
Phenyl Ether	8
Malathion	12.2
Atrazine	7.6
Dibenzothiophene	7.7
Dibutyl Phthalate	10
Fluoranthene	12
o,p'-DDD	0.3
Decachlorobiphenyl	6.4
Benzo(e)pyrene	30.4

TABLE 10

Data for Gel Permeation Chromatography

Resin:	BioBeads S-X8 (a polystyrene-divinylbenzene copolymer with an exclusion limit of 1000 as established with a straight chain polymer).
Resin weight:	100 g
Solvent:	CH_2Cl_2
Flow rate:	7 ml/min
Pressure:	5 psi
Injection:	from 2.1 ml sample loop

TABLE 11

Gel Permeation Chromatography of Standard Compounds

Compound Type	Standard	Percentage Found in G2 (100-140 ml)	Percentage Found in G3 (140-220 ml)
Alkanes	n-C_{16}	67	33
	n-C_{15}	0	100
	n-Decyl cyclohexane	2	98
Aromatics	Acenaphthene	0	100
	Acenaphthylene	0	100
	Anthracene	0	100
	Benzo(a)anthracene	0	100
	Benzo(b)fluoranthene	0	100
	Benzo(k)fluoranthene	0	100
	Benzo(e)pyrene	0	100
	Benzo(a)pyrene	0	100
	Benzo(ghi)perylene	0	100
	Biphenyl	15	85
	Chrysene	0	100
	Dibenzo(a,h)anthracene	0	100
	Dibenzothiophene	0	100
	2,6-Dinitrotoluene	0	100
	2,4-Dinitrotoluene	0	100
	Fluoranthene	0	100
	Fluorene	0	100
	Hexamethylbenzene	0	100
	Indeno(1,2,3-cd)pyrene	0	100
	1-Methyl-phenanthrene	0	100
	Naphthalene	0	100
	Phenanthrene	0	100
	Pyrene	0	100
	m-Quaterphenyl	30	70
	p-Quaterphenyl	30-50	50-70
	1,3,5-Triisopropylbenzene	30	70
Phenols	p-Chloro-m-cresol	0	100
	2,4-Dichlorophenol	0	100
	2,4-Dimethylphenol	0	100
	2,6-Dimethylphenol	0	100
	4,6-Dinitro-o-cresol	0	100
	2,4-Dinitrophenol	0	100
	2-Nitrophenol	0	100
	4-Nitrophenol	0	100
	Pentachlorophenol	0	100
	2,4,6-Trichlorophenol	0	100
	2,4,5-Trichlorophenol	0	100

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER

Table 11 (continued)
Gel Permeation Chromatography of Standard Compounds
Page 2

Compound Type	Standard	Percentage Found in G2 (100-140 ml)	Percentage Found in G3 (140-220 ml)
Phthalates	Bis(2-ethylhexyl)Phthalate	100	0
	Butylbenzyl phthalate	100	0
	Dibutyl phthalate	100	0
	Dimethyl phthalate	100	0
	Dioctyl phthalate	100	0
Esters	4-Bromophenyl ether	0	100
	4-Chlorophenyl ether	0	100
	Phenyl ether	10	90
Hydrazines	1,2-Diphenylhydrazine	0	100
Chlorinated hydrocarbons	Aldrin	0	100
	BHC's (α , β , γ)	0	100
	Captofol	65	35
	Chlordane	0	100
	2-Chloronaphthalene	0	100
	o,p'-DDD	0	100
	p,p'-DDD	0	100
	o,p'-DDE	0	100
	p,p'-DDE	0	100
	o,p'-DDT	0	100
	p,p'-DDT	0	100
	Dibenzo-p-dioxin	0	100
	3,3'-Dichlorobenzidine	0	100
	Dieldrin	0	100
	Endosulfan	0	100
	Endrin	0	100
	Heptachlor	0	100
	Heptachlor epoxide	0	100
	Hexachlorobenzene	0	100
	Kepone	0	100
	Trichlorodibenzo-p-dioxin	0	100
PCB's	Decachlorobiphenyl	0	100
	Aroclor 1242	0	100
Carbamates	Carbaryl	0	100
	Chlorpropham	0	100
	Aldicarb	100	0
	Butylate	50	50
	CDEC	0	100

Table 11 (continued).
Gel Permeation Chromatography of Standard Compounds
Page 3

Compound Type	Standard	Percentage Found in G2 (100-140 ml)	Percentage Found in G3 (140-220 ml)
Phosphate Esters	Temephos	100	0
	Malathion	100	0
	Dichlofenthion	80	20
	Trichlorfon	0	100
Triazines	Atrazine	50	50
	Ametryn	0	100

5. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

Fraction G3 must be further characterized and simplified for the detailed analysis by GC and GC-MS. Normal adsorption chromatography using silica gel could be used, but HPLC has certain advantages. They are as follows:

- Fraction volumes are smaller. This reduces the necessary concentration factor.
- Reproducibility is enhanced once the solvent program has been worked out (with silica gel the water content necessary for deactivation is difficult to control).
- There is less chance of sample contamination.

There are also some disadvantages, such as limited capacity and dead-time for recycling of the column. These, however, appear to be of secondary importance.

The methodology used for the HPLC separation was much influenced by Wise *et al*. (1977) and makes use of an analytical LiChrosorb NH_2 column with programming of solvent flow and polarity. Three fractions were derived. Fraction 1 is of mainly aliphatic nature but also contains some slightly polar chlorinated hydrocarbons. Fraction 2 contains compounds of slight to moderate polarity such as aromatics and more polar chlorinated hydrocarbons. Fraction 3, finally, contains polar compounds. Since some compounds again elute in more than one fraction (see Table 12), it is important that the experimental parameters of the HPLC (Figure 5) are kept constant and are carefully monitored to maintain reproducibility. With modern, fully automated instruments this is no problem.

Table 12 indicates that most organic compounds of concern can be expected to elute mainly in fractions 2 or 3. Thus, these two fractions were emphasized in the analysis.

TABLE 12

HPLC FRACTIONATION OF STANDARD COMPOUNDS
USING THE ELUTION SCHEME OF FIG. 5

Fraction 1	Fraction 2	Fraction 3
Normal Alkanes:	Normal Alkanes:	Amine:
n-C_{13}-n-C_{32} (92%)	n-C_{13}-n-C_{32} (8%)	Dicyclohexylamine
Polycyclic Aliphatics:	Polycyclic Aliphatics:	Aldehyde:
Cholestane (74%)	Cholestane (26%)	Nonanal
Chlorinated Hydrocarbons:	Aromatic Compounds:	Alcohol:
Aldrin (29%) Heptachlor (28%) p,p'-DDE (36%) o,p'-DDE (16%) p,p'-DDT (14%)	two rings to seven rings	Octanol
	Phthalates:	Triazine:
	Dimethyl phthalate Diethyl phthalate Dibutyl phthalate Bis(2-ethylhexyl)phthalate	Ametryn Atrazine
		Benzidine:
		3,3-dichlorobenzidine
	Carbamates:	Phenols:
	Butylate CDEC	2,6-dimethyl phenol 2,4-dichloro phenol 2,4,5-trichloro phenol
	Hydrazine:	
	1,2-Diphenylhydrazine	
	Ether:	
	Phenyl ether	

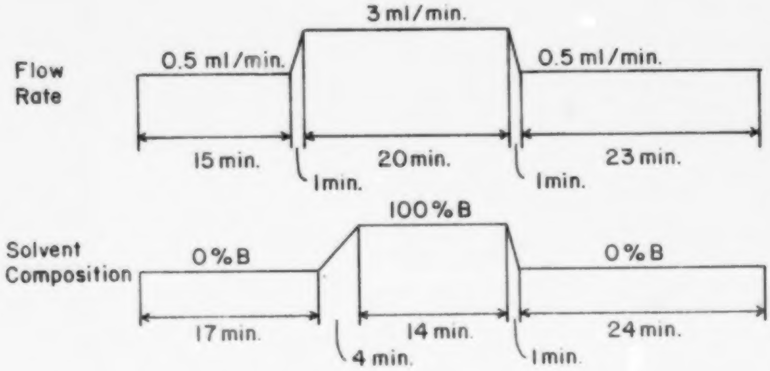
TABLE 12 (continued).

HPLC Fractionation of Standard Compounds Using the Elution Scheme of Fig. 5.

Fraction 1	Fraction 2	Fraction 3
	Chlorinated Hydrocarbon:	
	BHC's (α, β, γ)	
	Chlordane	
	Dieldrin	
	Endrin	
	Heptachlor epoxide	
	Aldrin (71%)	
	Heptachlor (72%)	
	p,p'-DDE (64%)	
	o,p'-DDE (84%)	
	p,p'-DDT (86%)	

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - NH_2 COLUMN

Solvents: A. n-Hexane, B. 2-Propanol


3 ml/min.
0.5 ml/min.
0.5 ml/min.
Flow Rate
15 min.
1 min.
20 min.
1 min.
23 min.
100% B
Solvent Composition
0% B
0% B
17 min.
4 min.
14 min.
1 min.
24 min.

Fractions Collected:

F_1 = 0-7.5 min.
F_2 = 7.5-19 min.
F_3 = 19-35 min.

Figure 5

6. GAS CHROMATOGRAPHIC ANALYSIS (GC)

GC analyses were performed on either modified Varian 2740 or Varian 3700 gas chromatographs. All instruments were equiped with approximately 27 m glass capillary columns, deactivated with silanol groups and statically coated with SE-52. (Grob *et al*., 1979; Godefroot *et al*., 1980). The internal diameter of these columns varied between 0.28 and 0.33 mm. The carrier gas was helium, adjusted to a flow of 3 ml/min, except for the EC detector where helium was replaced by nitrogen. Temperature programming extended from 75°C to 280°C at 6°C/min. Adsorption and "tailing" for each column were checked with special mixtures according to Grob (1978).

Before an analysis, a "daily standard" was routinely injected and analyzed to evaluate to response factors and retention. The composition of this standard is given in Table 13. Intermittently, an aromatic retention standard (Table 14) was injected to test the retention of a number of unsubstituted PNAs. Since these PNAs are found in most samples and can be identified either by mass spectrometry or by pattern recognition, a daily injection of the aromatic retention standard was found to be unnecessary.

After separation, output signals are generated by flame ionization detectors (FID) and electron capture detectors (ECD). All signals were recorded in analog form on a strip chart recorder and simultaneously digitized by Hewlett Packard A/D converters, from where they were fed to a H-P 3354B data system.

Each sample extract was analyzed in the following manner:

(a) The GPC fraction containing most of the pertinent information, fraction G3, after concentration to 0.2 ml (concentrated 400 times), was injected into capillary columns and detected by FID. An aliquot of this fraction was also injected with only two times concentration and detected by EC.

(b) Based on these chromatograms, a decision to further separate GPC fraction G3 on HPLC was made. In samples where the concentration of individual compounds was <(20-40) ppb (below the limit chosen for data interpretation), or where the composition was simple (only a few peaks with concentrations >(20-40) ppb present) there was no need to develop more detailed fractions. Complex samples containing many peaks >(20-40) ppb were separated by HPLC into 3 sub-fractions, G31, G32, and G33, and these were then reanalyzed by GC. All G32 fractions were injected twice, without and with a PNA standard superimposed, to derive aromatic retention indices.

TABLE 13

COMPOSITION OF THE DAILY STANDARD USED FOR GC

COMPOUND	CONCENTRATION (ng/μl)
Biphenyl	5.3
Butylate	21.4
CDEC	45.0
α-BHC	49.7
Aldrin	74.0
Ametryn	52.6
o,p'-DDD	42.5
Carboxin	45.8
Captofol	107.2
Decachlorobiphenyl	56.6
Benzo(a)pyrene	47.2

TABLE 14

AROMATIC RETENTION STANDARD

The following compounds are used to calculate the aromatic retention indices (ARI).

COMPOUND	ARI
Biphenyl	100
Phenanthrene	200
Pyrene	300
Chrysene	400
Perylene	500
Benzo(ghi)perylene	600

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

Every GC analysis generated a raw file in the H-P 3354B that was further processed by suitable software. This processing will be described in the chapter on Data Processing.

7. GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

Of the numerous peaks commonly encountered in fractions derived from sediment or tissue samples, only some fall into the category of "toxic organic compounds." Many of these GC peaks relate to compounds that, at the concentrations they are encountered, are of little concern. For this reason, there needs be a mechanism that allows one to distinguish between the two types. In the molecular weight range up to about 520, there is little one can do but identify the compounds. This requires a thorough analysis by GC-MS. Another approach is the use of specific chromatography to remove unwanted compound types, such as removal of large biogenic (steroid and triterpenoid) molecules by GPC.

The detailed qualitative analysis includes the following steps:

(a) Separation of the sample on a glass capillary column similar to those used for the GC analysis.

(b) Scanning of the mass range from m/e = 51 to m/e = 517 (one scan per 2.8 sec.) and storage of the mass spectra on a disc.

(c) Reconstruction of a chromatogram from recorded ionic data.

(d) Construction of a chromatogram for specific fragments that either are characteristic of known toxic compounds or are known to occur repetitively in samples (although their molecular structure may not be identifiable).

(e) Printout of mass spectra for peaks detected in (d) and, if possible, identification of the associated structures. Where structural isomerism can lead to almost identical fragmentation for different isomers, combination of mass spectral information with GC retention data is necessary for identification.

(f) Printout of mass spectra for all peaks in the reconstructed chromatogram that in (e) have been missed.

(g) Identification of the compounds in (f).

The structural information must now be transferred from the reconstructed chromatogram to the FID chromatogram. Since the chromatograms are plotted on different scales, it is often difficult to recognize common features by comparison of patterns. To assist in this task, an additional chromatogram resulting from a D/A conversion of data fed to the computer is plotted on a scale similar to the FID output. The most powerful method of correlation, however, is based on the use of relative retention indices.

A summary of the chemical methodology is presented in Figure 6.

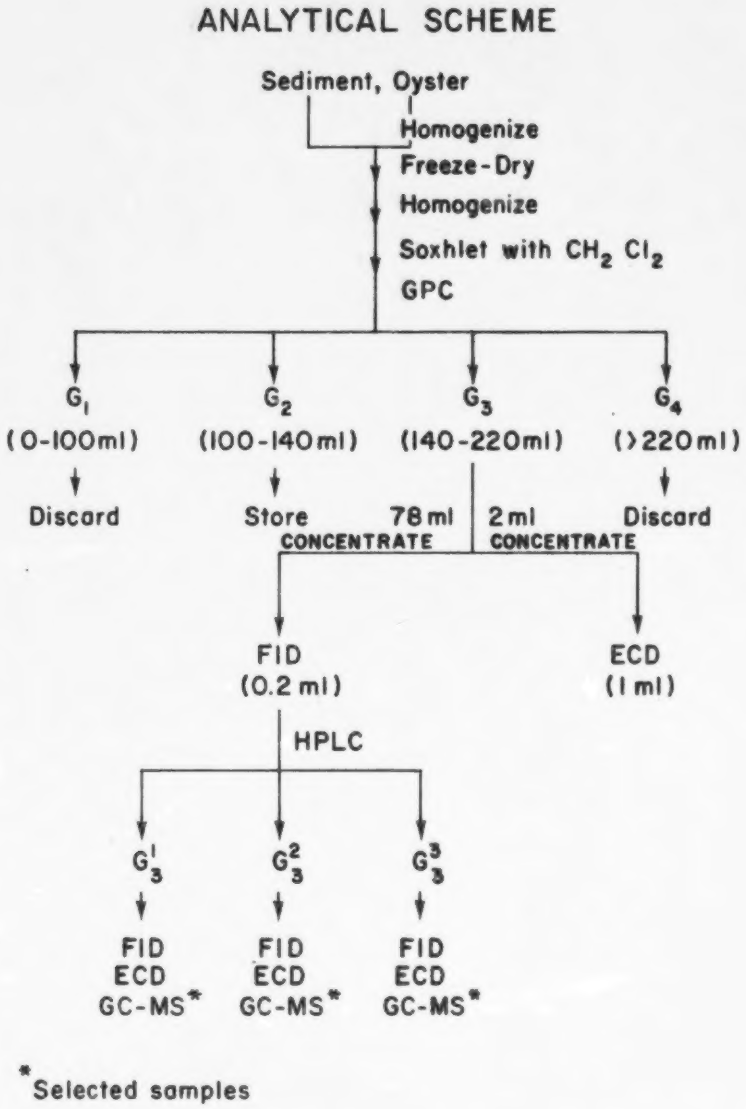

ANALYTICAL SCHEME
Sediment, Oyster
Homogenize
Freeze-Dry
Homogenize
Soxhlet with CH2 Cl2
GPC
G1
(0-100ml)
Discard
G2
(100-140ml)
Store
G3
(140-220ml)
78ml
CONCENTRATE
2ml
CONCENTRATE
G4
(>220ml)
Discard
FID
(0.2ml)
ECD
(1ml)
HPLC
G3 1
FID
ECD
GC-MS*
G3 2
FID
ECD
GC-MS*
G3 3
FID
ECD
GC-MS*
*Selected samples

FIGURE 6

8. USE OF COMPUTER SYSTEMS FOR DATA REDUCTION AND DISPLAY

A Hewlett Packard 3354B laboratory automation system served to collect, process and store gas chromatographic data using system software and basic programming.

Chromatographic output signals were integrated over half-second intervals, digitized, and stored as raw files on a magnetic disc. Software for the following operations is available:

(a) Calculate concentrations of GC peaks by reference to internal or external standards, discriminate against peaks with less than a predetermined minimum concentration and calculate relative retention indices (an aromatic retention index (ARI) and/or a pesticide retention index (PRI)).

(b) Display both processed and normalized data on the H-P 3354B system console (H-P 2648A terminal) and line printer (H-P 9866B).

(c) Plot bar-graphs from processed data on a Tektronix 4662 flat bed plotter and on the H-P 2648A terminal, the latter for visual inspection only.

(d) Plot chromatograms from raw data on a Tektronix 4662 flat bed plotter (adapted from Overton *et al.*, 1979) and on the H-P 2648A terminal, the latter again for visual inspection.

(e) Tabulate all peaks in the reconstructed chromatograms from GC-MS, giving their position relative to the scan number and ARI. The number of ions at the maximum and the four largest peaks in the mass spectrum, are also included.

(f) Compare GC peaks (defined by their retention indices) in samples collected at a particular station at different times and flag samples in which the concentrations of a given peak either are 10 times larger or smaller than the concentration in the first sample. If a sample does not contain a particular peak detected in an earlier sample, it is assumed that the peak is present below a 1 ppb threshold and a ratio based on this assumption is printed out. However, if a peak is present in the later sample, but cannot be found within the retention window in the earlier sample, it is listed as a new compound if its concentration exceeds 50 ppb.

(g) Compare peaks (defined by a retention index) in gas chromatograms of samples from all stations, flag stations in which the concentrations of some peaks exceeds 50 ppb and provide a printout.

(h) Search data files for peaks eluting within a specified retention index window and list sample identification codes, retention indices and concentrations.

A schematic representation of the data processing is given in Figure 7.

The first four software packages are system software or are written in BASIC on the H-P 3354B system. Package (e) is a FORTRAN program (C. Hein, 1980) run on the MS data system. Packages (f) to (h) are written in FORTRAN using RATFOR pre-processor software and run on an IBM 370/156 mainframe using data files on magnetic tapes produced by H-P 3354B software.

Software package (a) quantities peaks in the chromatograms by reference to an internal or external standard (originally p-quaterphenyl, but later changed to 1,1'-binaphthyl), to remove all peaks of less than a preselected concentration, and to calculate retention indices using appropriate marker compounds. Since specialized retention indices define the position of a toxic compound in the chromatogram much more precisely (Bieri, 1977; Bieri et al., 1979; Lee et al., 1979) than absolute retention data, they are important for interpolation purposes in samples that have not been analyzed by GC-MS). A listing of ARIs established within this project and a comparison with published data (Lee, et al., 1979), after conversion from their retention standards to ours is given in Table 15.

Package (b) allows a visual check and review of data in storage.

Package (c) generates a chromatogram-like display in which peak concentrations are displayed in bar-graph form. Compared to the analog chromatograms (Figure 8a), complexity is dramatically reduced by the elimination of peaks corresponding to below-threshold concentration (Figure 8b). The positions of the peaks are better defined, and since the unresolvable background is removed, baseline drifts are absent in the bar-graph display. Every line in this bar-graph thus conveys relevant information, with the position of the bar in the chromatogram relating to molecular structure and the height representing concentration (semi-quantitative).

Package (d) allows the reproduction of chromatograms from stored digital data. The chromatograms in this report have been generated by this software package. Such chromatograms are particularly useful because they can be scaled to concentration. An additional advantage of this program is that it delivers chromatograms ready for publication.

Package (e) serves mainly to simplify and improve the quality of the mass spectrometric analysis. It also provides an important link to the data obtained by the FID, since ARIs are independently calculated from the

Figure 7

FLOW DIAGRAM FOR USE OF COMPUTER PROGRAMS

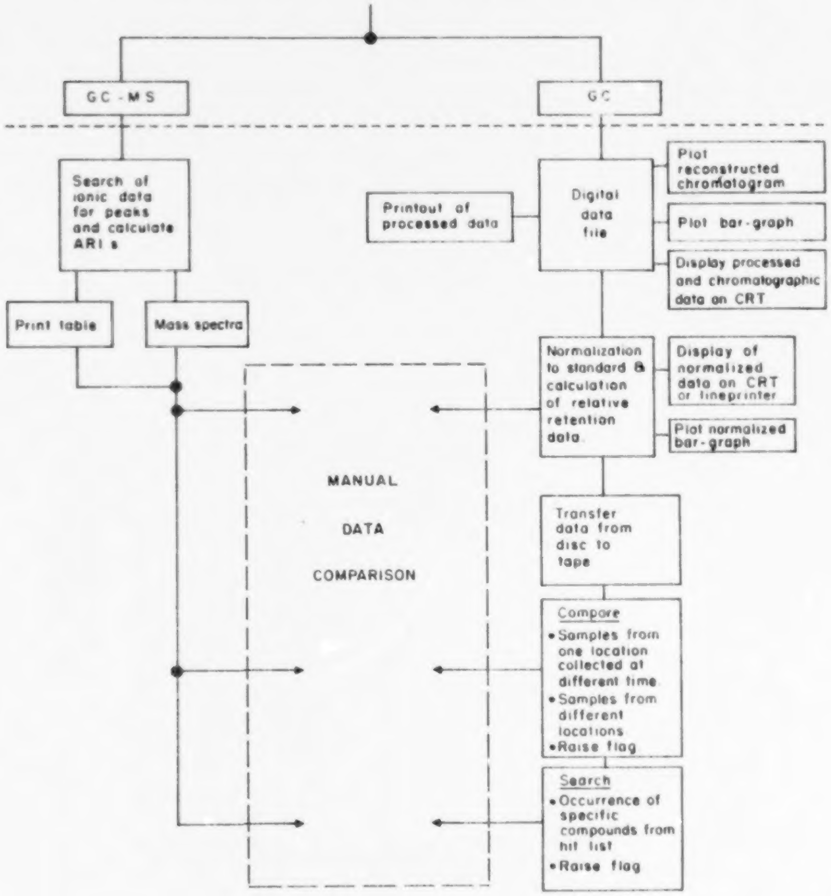

GC-MS
GC
Search of ionic data for peaks and calculate ARI s
Print table
Mass spectra
Printout of processed data
Digital data file
Plot reconstructed chromatogram
Plot bar-graph
Display processed and chromatographic data on CRT
Normalization to standard & calculation of relative retention data.
Display of normalized data on CRT or lineprinter
Plot normalized bar-graph
MANUAL DATA COMPARISON
Transfer data from disc to tape
Compare
•Samples from one location collected at different time.
•Samples from different locations
•Raise flag
Search
•Occurrence of specific compounds from hit list
•Raise flag

TABLE 15

AROMATIC RETENTION INDEX

COMPOUND	CHANNEL 4 AVERAGE	CHANNEL 4 S.D. (N=3)	CHANNEL 8 AVERAGE	CHANNEL 8 S.D. (N=3)	M. Lee et al.‡ AVERAGE	M. Lee et al.‡ S.D. (N=3-8)
PNA						
2,6-Dimethyl Naphthalene	106.2	0.1	105.8	0.2	105.5	0.2
2-Methyl Biphenyl	106.4	0.2	105.7	0.3	107.3	0
1,3-Dimethyl Napthalene	110.6	0.1	109.6	0.3	109.5	0.2
1,4-Dimethyl Naphthalene	115.6	0.1	114.2	0.3	114.6	0.2
1,5-Dimethyl Naphthalene	115.9	0	114.9	0.1	116.7	0.2
*Acenaphthylene	117.0	0.1**	116.0	0.1**	116.2	0.2
Hexamethyl Benzene	119.4	0.1***	118.1	0.2***		
Acenaphthene	128.9	0.2	127.4	0.3	126.2	0.1
3-Methyl Biphenyl	131.6	0.2	130.4	0.2	131.4	0.2
2,3,5-Trimethyl Naphthalene	148.6	0.1	146.8	0.2		
*Fluorene	152.2	0.3**	150.7	0.3**	151.8	0.2
3,3'-Dimethyl Biphenyl	157.2	0.3	156.0	0.6	157.4	-
1-Methyl Fluorene	183.1	0.1	182.5	0.1	183.4	0
Dibenzothiophene	193.5	0.1	193.4	0.1	193.7	0
*Anthracene	203.1	0.1**	203.0	0.1**	203.3	0.1
1-Phenyl Naphthalene	229.0	0.2	229.1	0.6	229.7	0.1
2-Methyl Anthracene	241.5	0.1	241.6	0.1	242.1	0.1

Table 15 (continued).

1-Methyl Phenanthrene	246.2	0.2	246.2	0.1	245.5	-
9-Methyl Anthracene	256.4	0.1	256.5	0.1	256.9	0.2
2-Phenyl Naphthalene	262.0	0.1	262.6	0.2	263.6	0.1
3,6-Dimethyl Phenanthrene	272.0	0.1	272.8	0	273.9	0.1
*Fluoranthene	285.6	0.1**	285.9	0.1**	285.9	0.2
Benzo(a)Fluorene	331.0	0.2	331.8	0.3	331.8	0.1
Benzo(b)Fluorene	336.3	0.1	336.8	0.2	337.2	0.2
9-Phenyl Anthracene	391.6	0.1	392.4	0.3	392.6	-
*Benzo(a)Anthracene	397.0	0.1**	397.3	0.1**	396.9	0.1
Benzo(b)Fluoranthene	474.3	0.1	474.7	0.2	474.2	0.5
*Benzo(k)Fluoranthene	475.9	0.2	476.5	0.1	475.7	-
Benzo(e)Pyrene	491.3	-	491.9	0.7	490.3	0.2
*Benzo(a)Pyrene	494.3	0.5**	494.2	0.2**	495.1	-
*Indeno(1,2,3,-cd)Pyrene	577.7	0.1**	582.9	0.4**	556.9	0.1
p-Quaterphenyl	564.8	0.2			570.9	0.4
*Dibenz(a,h)anthracene	587.3	0.7	589.5	0.7	587.0	-

---

‡ M. L. Lee, D. L. Vassilaros, C. M. White and M. Novotny, Anal. Chem. 51, 768 (1979)

*: EPA 129 Priority Parameters

**: n=6

***: n=24

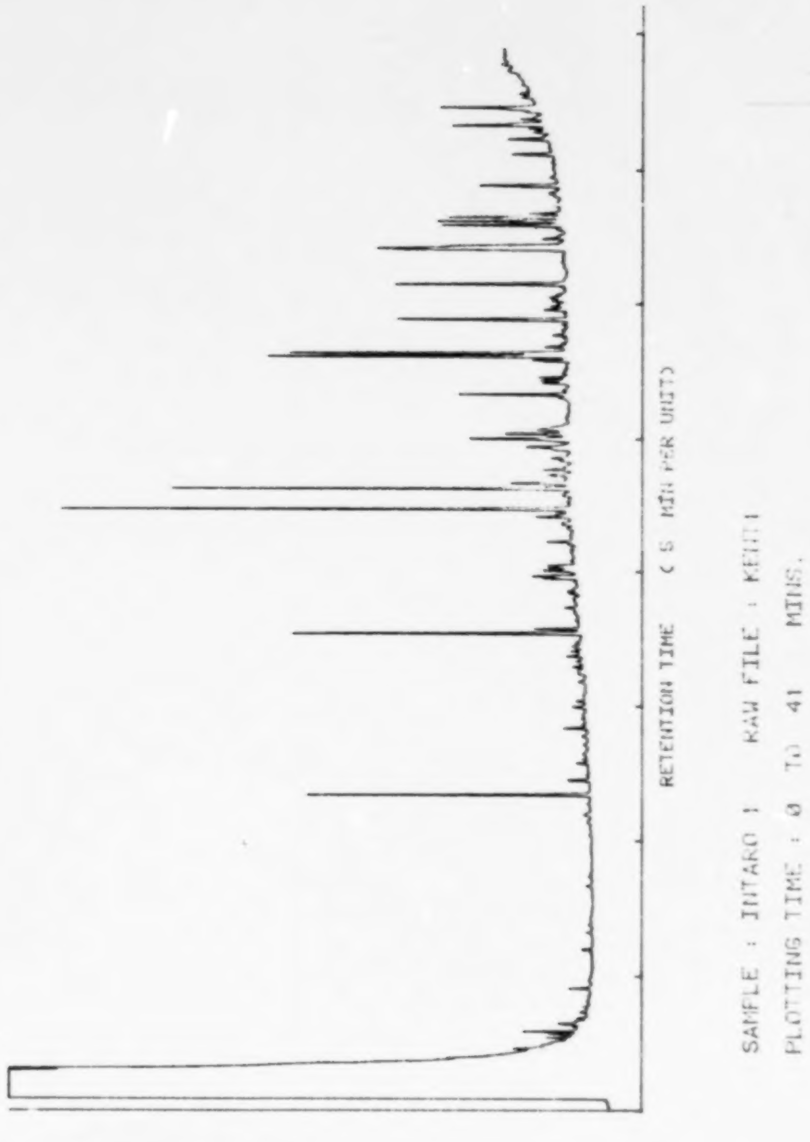


Figure 8a. Computer-generated displays of results. Gas chromatogram reconstructed from digital data stored on disc.

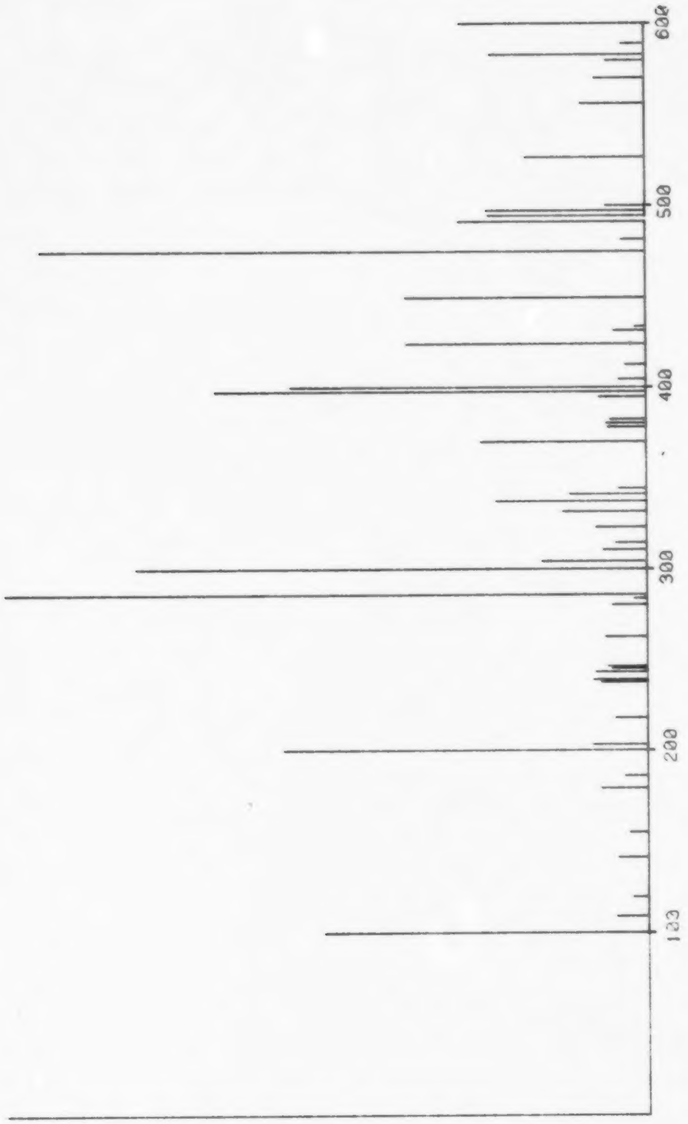


Figure 8b. Computer-generated displays of results. Bar graph of the same data set after processing to replace time with aromatic retention indices and elimination of compounds present below threshold concentration.

mass spectrometeric data. The program is self-running and continuously lists peak maxima present in the ionic data (Table 16). It does, however, require the presence of a positive and negative slope in sequence to respond with a printout; that is, two peaks eluting so close that the slope changes sign only once would be listed as one peak, although changes in the magnitude of the slope may be clearly visible.

The last three packages address the data bank with specific questions such as:

> Are there any sampling locations in which a particular compound is present above a given concentration?
>
> Are there any sampling locations at which a given compound is particularly prominent?
>
> Are there any significant changes in the concentrations of a given compound at a particular station as a function of time?

Package (f) serves to address any substantial changes in the sample composition at a specified location. Any new compound of greater than the minimum specified concentration added between two samplings at the same location would immediately be picked up by this program. Likewise, in a specified location any dramatic change (by a factor of 10 or more) in the concentration of compounds between two samplings ordinarily present would be flagged.

Package (q) allows similar inquiries for the total data set. It flags the presence of unusual compounds above the specified minimum concentration in a particular station or area. This program detects the introduction of new compounds to the system being studied.

Package (h) searches the data base for compounds characterized by a retention index window (ARI ± a number of ARI units that depends on the precision and accuracy of the relative retention index). In addition to a printout of the data search, this information can also be delivered as a bar graph, with the height of the bar representing concentration and the position of the bar representing the station location.

TABLE 16

Computer-generated output from GC-MS raw data.

<(X)> EP880 <(X)>

2-25-5 Q32+NAPHTHALENE

SCN#	PEAK RRI	HEIGHT	MOST ABUNDANT FRAGMENT MASSES 1ST	2ND	3RD	4TH	COMPOUND
54	.0	6333.	128	129	127	64	Naphthalene (STD)
104	55.0	6036.	142	141	115	143	Me - Naphthalene
112	63.7	2298.	142	141	91	115	Me - Naphthalene
145	100.0	3340.	154	153	152	155	Biphenyl
151	103.4	1463.	141	156	91	92	Et - Naphthalene
156	106.3	7472.	156	141	155	77	C_2 - Naphthalene
163	110.3	6170.	156	141	155	157	C_2 - Naphthalene
165	111.1	2879.	156	141	155	69	C_2 - Naphthalene
167	112.6	687.	91	154	153	92	1,4 - Dihydro - 1,4 - Ethenonaphthalene
172	115.3	2974.	156	141	155	91	C_2 - Naphthalene
176	117.5	3764.	152	151	76	153	Acenaphthylene
179	119.3	1681.	156	141	91	83	C_2 - Naphthalene
182	121.0	639.	69	91	55	109	Mixture
193	127.0	3333.	153	154	152	76	Acenaphthene

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD BEGIN SECTIONS HERE
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PART II

6 1/2"
9 1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

RESULTS

It is impossible to incorporate and discuss the vast amount of data we have collected in this report and at the same time make it readable. A complete data set for station 23 is found in Appendix I to demonstrate this problem. As a compromise, we present only data that we have judged to be of significance and refer the reader interested in more detail to a number of appendices or to the complete data bank which is provided on tape. Reference to the appendices will be made at appropriate places in the text.

1. PROCEDURE BLANKS

In the discussion of the solvent extraction, it was pointed out that CH_2Cl_2 under reflux conditions also is not ideal and leads to the generation of artifacts. They show up in all of the twelve procedural blanks, in both FID and ECD chromatograms (Figures 9 and 10). The chromatograms are on an expanded scale (normalized to the largest, non-solvent peak). Mass spectrometry clearly indentifies the largest of these peaks as chlorinated compounds containing five or six chlorine atoms (Figures 11-13). Attempts to identify the structures have not been successful, but we know that they are not aromatic and probably also contain one nitrogen atom. Although the concentration of some of these artifacts in some blanks can be as high as about 40 ppb and for this reason would be expected to be clearly visible in sample extracts, we have not been able to find any of these artifacts in any of the samples.

These artifacts were not present in solvents. We also established that they are not contaminants introduced by glassware (flasks, test tubes, pipettes, etc.) or septa. An experiment in which CH_2Cl_2 was exposed to the laboratory atmosphere also gave negative results. We must thus conclude that these artifacts are generated during the Soxhlet procedure and that the presence of organic compounds from samples inhibits or suppresses their generation. Soxhlet refluxing of solvent in the presence of light appears to stimulate the formation of many artifacts, but the major artifacts are also present when the Soxhlet reflux is carried out in the dark. More research is needed to understand these discrepancies.

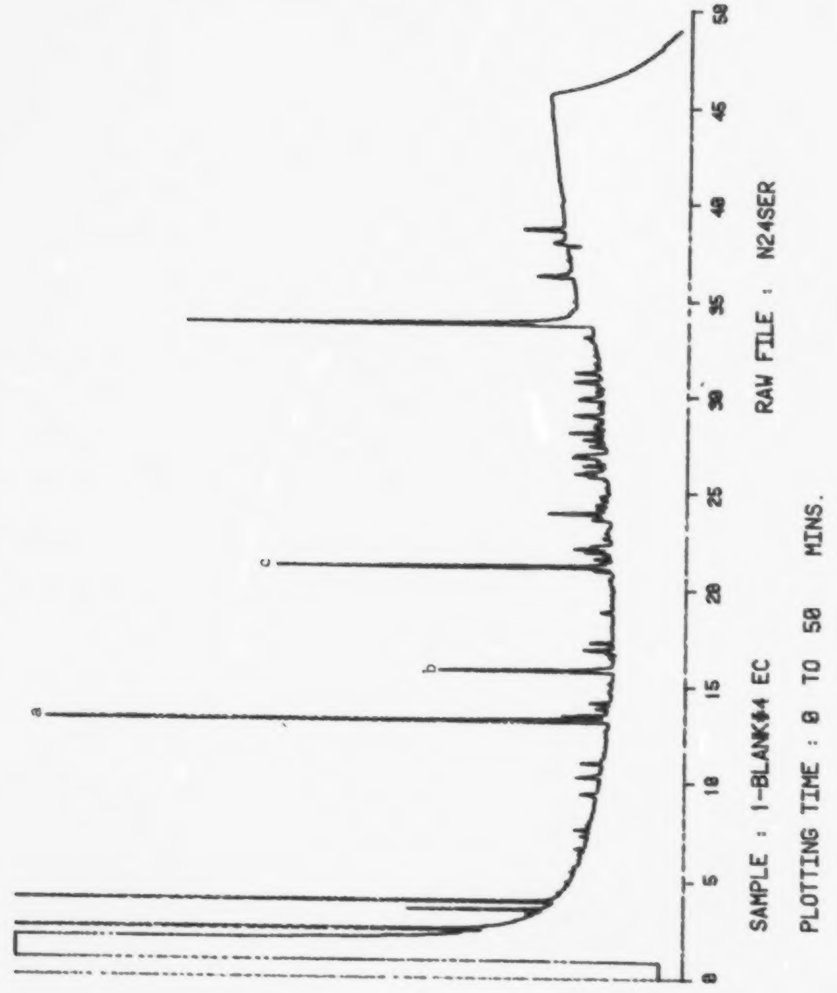


Figure 9. Chlorinated artifacts in procedural blanks. Blank chromatogram, electron capture detector. Artifacts discussed are labeled a, b and c.

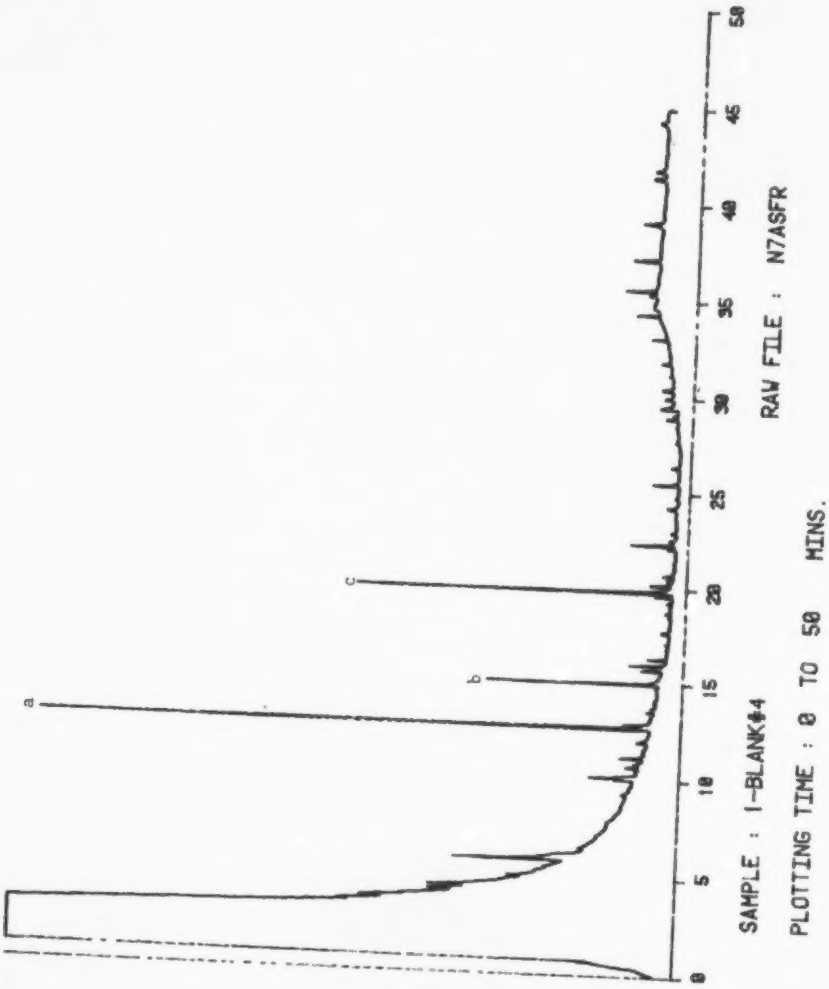


Figure 10. Chlorinated artifacts in procedural blanks. Blank chromatogram, flame ionization detector.

FIGURE 11

Chlorinated Artifacts in Procedural Blanks

Mass Spectrum of Compound A

```
SEQUEN     44     PAGE      1

DRAW MS
GC ID EP    896   DATE  12/17/80
AQRATE        6   SCTIME       1   RESPWR   500
HIMASS      500   THRESH       1

1-BLANK#4 + S8

IGNORE     0,     0,     0,    0
%SCALE  100   #AMU'S   200      HRDCPY     NO
SUBTR     0   BASEPK     0      SCAN #   185
BKGRND  187
BASE    2439 %2** 0   % TOTAL IONIZ.      9
```

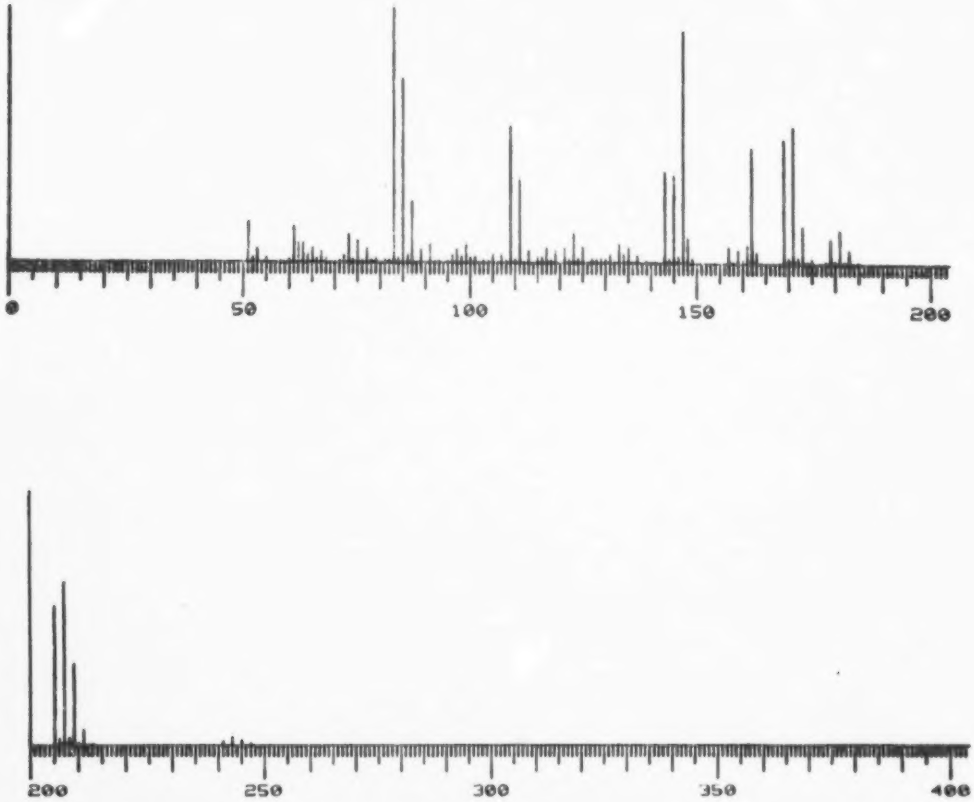


FIGURE 12

Chlorinated Artifacts in Procedural Blanks

Mass Spectrum of Compound B

```
SEQUEN     44    PAGE      3
GCID  EP  896  1-BLANK#4 + S8

IGNORE     0,      0,      0,      0
%SCALE   100    #AMU'S    200      HRDCPY      NO
SUBTR      0    BASEPK      0      SCAN #    237
BKGRND   235
BASE     557 #2## 0    % TOTAL IONIZ.       12
```

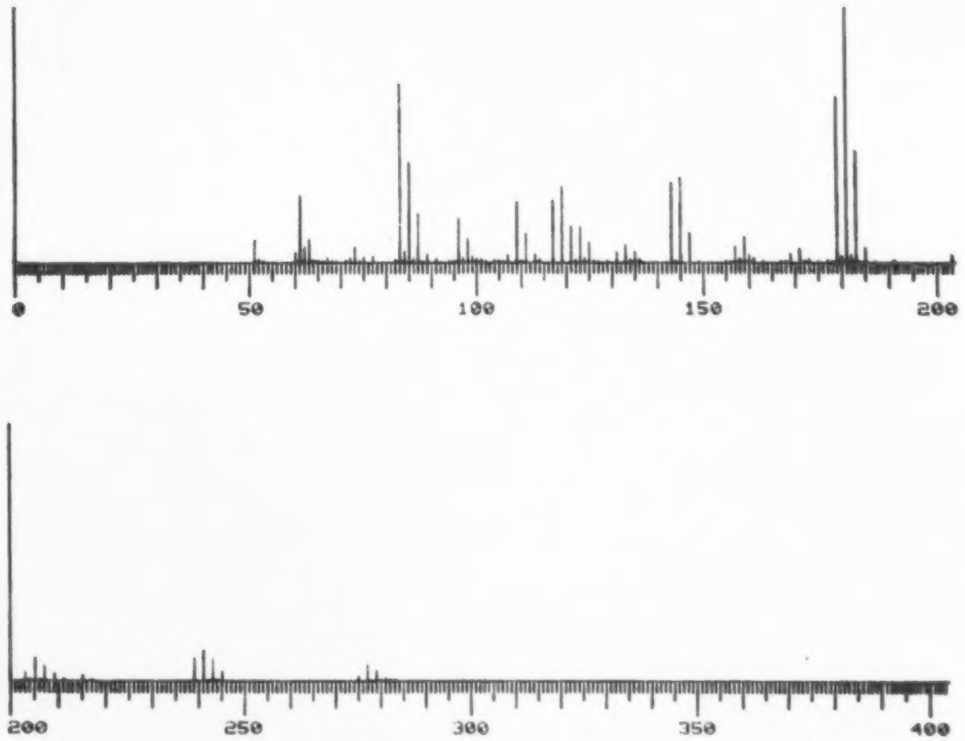


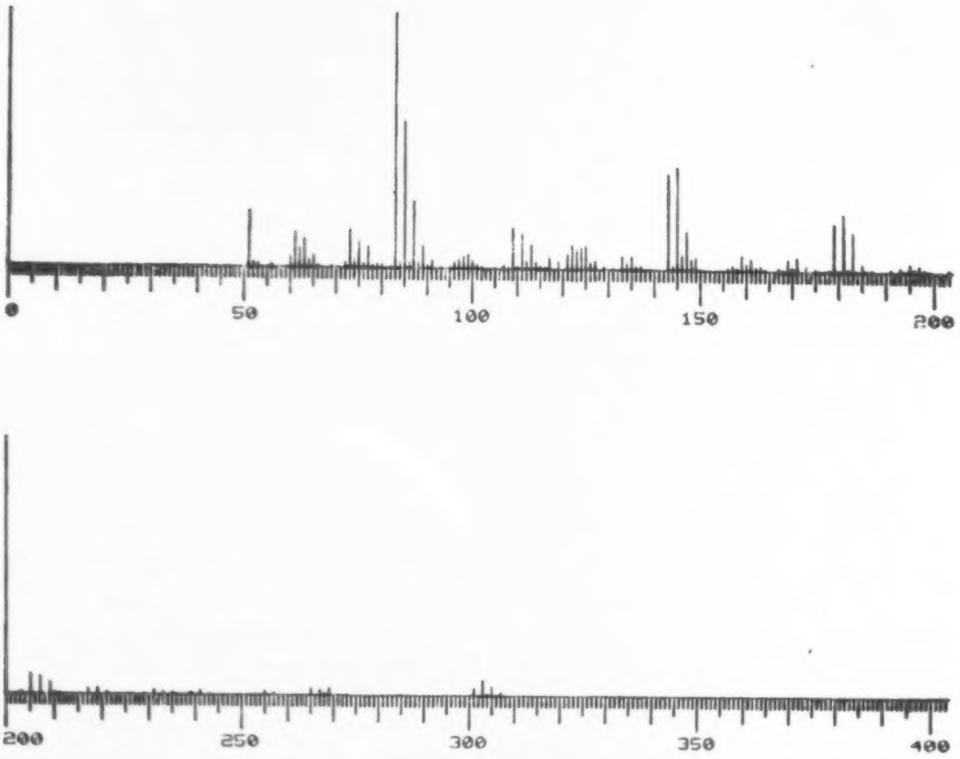
FIGURE 13

Chlorinated Artifacts in Procedural Blanks

Mass Spectrum of Compound C

```
SEQUEN     44    PAGE      5
GCID  EP  896  1-BLANK#4 + S8

IGNORE     0,      0,      0,    0
%SCALE   100    #AMU'S    200      HRDCPY      NO
SUBTR      0    BASEPK      0      SCAN #    345
BKGRND   344
BASE     933 #2** 0   % TOTAL IONIZ.       13
```



2. VARIABILITY OF MAJOR ORGANIC POLLUTANTS IN SEDIMENT SAMPLES

To assess the variability of pollutants in sediments, ten replicate samples were collected at the mouth of the York River (Station 05S). Each was separately processed and analyzed. The statistical evaluation of these analyses is shown in Table 17. PNAs only could be compared because they were by far the largest peaks present in the chromatograms--a situation that is not uncommon in sediments (Giger and Blumer, 1974; Bieri *et al.*, 1978; Hites *et al.*, 1981). The homogeneity found in these replicate analyses is expected because of the general distribution pattern of PNAs.

TABLE 17

O5S-Replicates (N=10)
Reproducibility of Major Identified Peaks

Compound	ARI	Conc. (ppb=±SD)
Phenanthrene	200	4.6±3.4
Fluoranthene	285.5	12.8±5.3
Pyrene	300	13.4±5.1
Benz(a)anthracene	397.1	7.6±2.9
Chrysene	400	12.6±4.8
Benzo(e)pyrene	491.4	10.7±3.6
Benzo(a)pyrene	494.4	11.1±3.8
Perylene	500	16.4±7.9
Indeno(1,2,3,-cd)pyrene	578	14.7±5.0
Benzo(ghi)perylene	600	13.1±5.4

3. PROBLEMS ASSOCIATED WITH INSUFFICIENT RESOLUTION AND SPECIFIC DETECTOR RESPONSE

A. Evaluation of FID Chromatograms

Almost all samples that contain high concentrations of organic compounds also are characterized by very complex chromatograms. Although the best available methodology was applied to get chromatograms of highest resolution, only partial separation was achieved in many peaks. The presence of an unresolvable complex envelope (UCM) indicates areas where separation is utterly insufficient. In such chromatograms, peak integration by electronic means or by computers has always been a problem. In this case, the available integration software of the H-P 3354B, although it is quite flexible, is incapable of coping with the complexity of the chromatograms. As a result, discrepancies were noted when the integrated output was compared with the chromatograms.

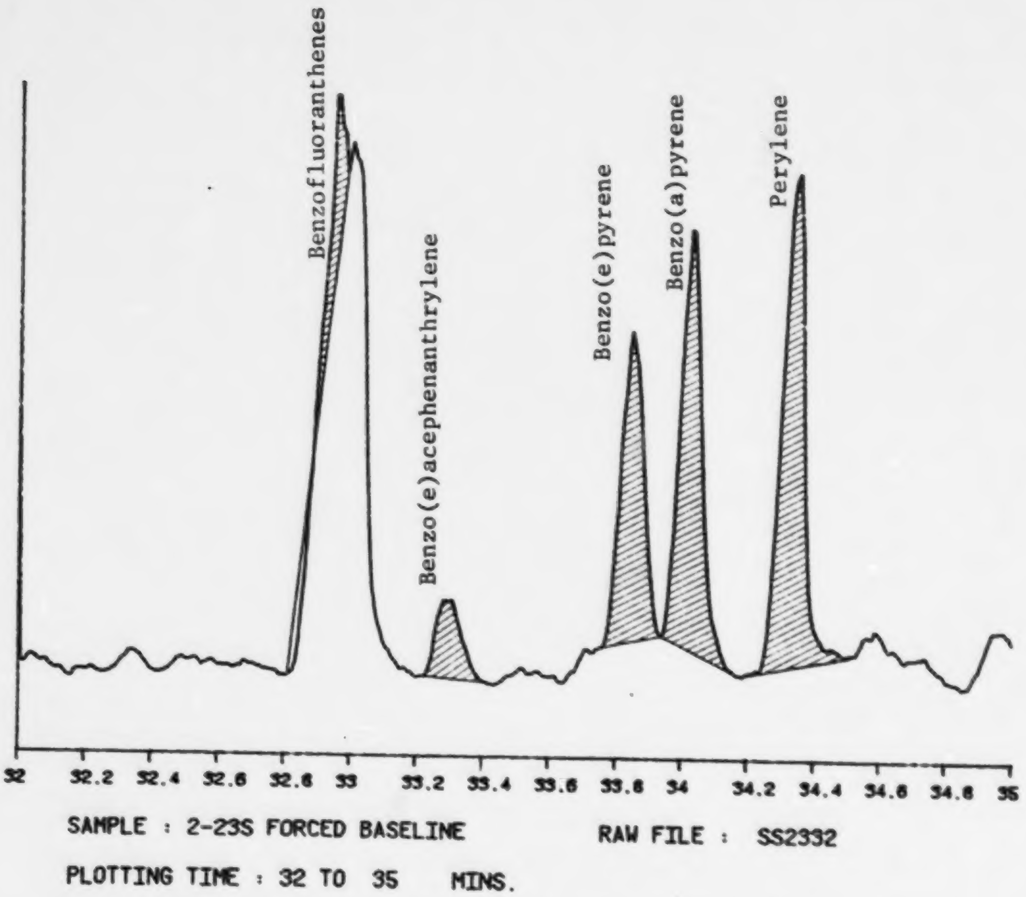
A typical example is benzofluoranthene. This compound has three isomers (benzo(b)fluoranthene, benzo(j)fluoranthene and benzo(k) fluoranthene) that elute very close to each other. The integration of this peak can go wrong in two different ways, as demonstrated in Figures 14a and b. If the baseline is held constant over the interval containing benzo-fluoranthene, the peak area is too large because some of the unresolvable envelope is included. If the baseline is forced as in Figure 14a, the integrated area is much to small. In the latter example, the computer even disregarded the second half of the split benzofluoranthene peak. Either increased or decreased column resolution would have permitted a correct determination of the total area occupied by benzofluoranthene isomers.

There is a method available to correct such discrepancies in future analyses. It is based on vertical splitting as in Figure 14c, but with a baseline that represents a polynomial approximation to the UCM. Software to implement this method has now been developed.

It clearly is very difficult to find a correct method to derive quantitative data from chromatograms that are as complex as those discussed here. The corrective step mentioned above promises to be superior to what was available for the semi-quantitative data in this report, but there still will be limitations to achievable accuracy.

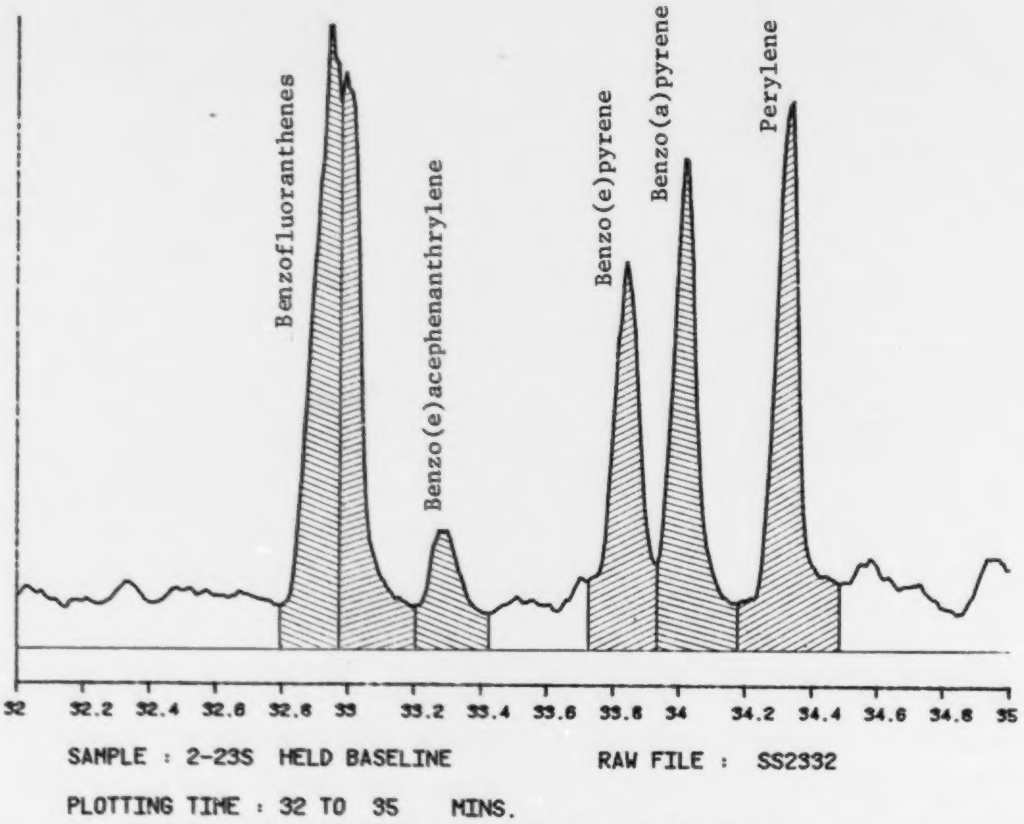
B. Evaluation of ECD Chromatograms

Three well-known factors contribute to make the evaluation of ECD chromatograms difficult:



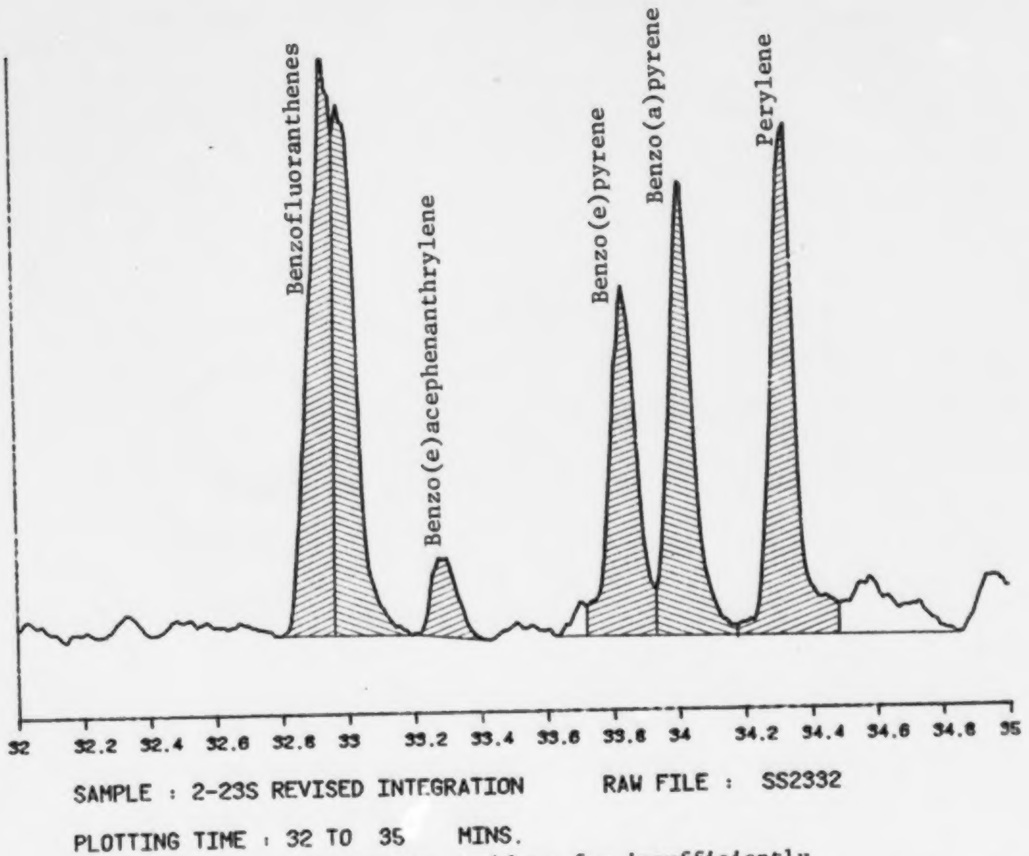
Demonstration of integration problems for insufficiently resolved peaks, forced baseline.

Figure 14a



Demonstration of integration problems for insufficiently resolved peaks, vertical splitting.

Figure 14b



Demonstration of integration problems for insufficiently resolved peaks, vertical splitting and improved baseline approximation.

Figure 14c

1. The ECD response is not as uniform as the FID, but varies with the number of substituted halogens present. Thus, any conversion of area units to concentration via the use of a particular internal or external standard cannot be expected to be generally applicable.

2. The response of the ECD is not limited to the presence of halogen. Organic compounds containing O, S, or P and certain unsaturated hydrocarbons may give substantial EC signals.

3. The sensitivity of the ECD for some halogenated compounds is much higher than the sensitivity of the GC-MS system. Where the concentration of such compounds is too low to generate good mass spectra, confirmation of a structure identification based on retention is impossible.

While factor 1 affects only the accuracy of a stated concentration, factors 2 and 3 contribute to serious discrepancies. Searching the data bank for specific chlorinated hydrocarbons or pesticides within their characteristic retention window indicates the presence of such compounds, but confirmation by GC-MS often is not possible. An example is given in Table 18, where ECD data bank for sediments was searched for p,p'-DDT. The table contains two outstanding concentrations: 3,060 ppb for station 2-19-S and 13,400 ppb for station 2-27-S. A corresponding search for p,p'-DDT in the FID data bank (Table 19) again indicates a concentration maximum in station 2-27-S, but the mass spectrum (Figure 15) shows no evidence for the presence of p,p'-DDT. Both, mass spectrum and retention, identify this compound as benzo(b)naphto(2,1-d)thiophene. It is this sulfur-bearing compound that contributes to most of the peak at the position of p,p'-DDT in the ECD chromatogram. The maximum in sample 2-19-S, however, is real, as documented by the mass spectrum (Figure 16, with some hexachlorobiphenyl superimposed) and the retention parameter.

While p,p'-DDT has been singled out for this discussion, similar caution is suggested for other chlorinated hydrocarbons.

TABLE 18

Search for p,p'-DDT (PRI-window 224.0-225.3) in ECD Data Files

STATION	PRI	CONC (ppb)
1-03-S	225.3	3.3
1-05-S	225.3	4.7
1-14-S	224.1	9.8
1-17-S	225.1	4.0
1-20-S	225.3	1.1
1-21-S	225.2	3.1
1-22-S	225.3	3.4
1-24-S	224.7	1.2
1-25-S	225.1	1.5
1-26-S	224.1	25.8
1-27-S	224.2	13.0
2-01-S	225.1	2.0
2-08-S	224.0	2.6
2-09-S	224.3	8.9
2-11-S	224.2	8.4
2-12-S	224.1	6.2
2-13-S	225.0	17.4
2-17-S	224.1	29.2
2-18-S	224.3	26.9
2-19-S	225.0	3060.0
2-20-S	225.1	6.6
2-22-S	225.2	1.9
2-23-S	225.0	5.7
2-24-S	225.1	10.2
2-26-S	224.3	6.7
2-27-S	224.3	13400.0

TABLE 19

Search for p,p'-DDT (ARI-window 375-381) in FID Data Files

STATION	ARI	CONC (ppb)
1-01-S	377.6	8.6
1-01-S	380.1	1.7
1-03-S	378.0	3.2
1-05-S	378.1	3.9
1-08-S	380.4	3.7
1-15-S	375.0	2.6
1-15-S	380.5	2.7
1-17-S	378.0	3.0
1-17-S	380.6	1.5
1-18-S	377.9	2.6
1-19-S	377.8	4.8
1-19-S	380.5	6.6
1-20-S	377.7	11.7
1-20-S	380.4	27.3
1-21-S	377.6	34.8
1-21-S	380.1	11.6
1-22-S	377.6	29.8
1-22-S	380.3	6.6
1-23-S	377.7	44.3
1-23-S	380.1	97.0
1-24-S	378.0	5.4
1-25-S	378.2	7.3
1-25-S	380.7	1.1
1-26-S	377.5	51.4
1-26-S	380.0	8.6
1-27-S	375.0	66.7
2-03-S	377.8	10.6
2-03-S	380.8	10.3
2-08-S	378.0	2.2
2-08-S	380.6	1.5
2-13-S	377.8	2.4
2-15-S	377.9	2.0
2-17-S	378.2	3.9
2-18-S	378.0	3.0
2-19-S	379.9	2713.0
2-20-S	378.2	4.4
2-21-S	377.9	18.6
2-21-S	381.0	46.4
2-22-S	377.9	24.8
2-23-S	377.6	41.7
2-23-S	380.3	14.0
2-24-S	378.2	8.8
2-25-S	376.6	1.7
2-25-S	377.3	2.2
2-25-S	380.5	1.8
2-26-S	377.9	8.1
2-26-S	378.8	1.3
2-26-S	380.6	4.6
2-27-S	375.6	268000.0

FIGURE 15

Mass spectrum of a peak identified in a computer search of the EC files as p,p'DDT. The mass spectrum clearly shows that this is a misidentification, caused by a high response of benzo(b) naphtho(2,1-d)thiophene in the EC detector, and elution of this compound is the same retention window as p,p'-DDT.

```
SEQUEN     47     PAGE      1

DRAW MS
GC ID EP     906    DATE  12/18/80
AQRATE         6    SCTIME      1    RESPUR    500
HIMASS       500    THRESH      1

2-27S G32 REINJECT TO CHECK SMALL PEAKS

IGNORE     0.      0.      0.      0
%SCALE   100    $AMU'S    200       HRDCPY      NO
SUBTR      0    BASEPK      0       SCAN $    508
BKGRND   506
BASE    5227 $2$$ 0    % TOTAL IONIZ.      29
```

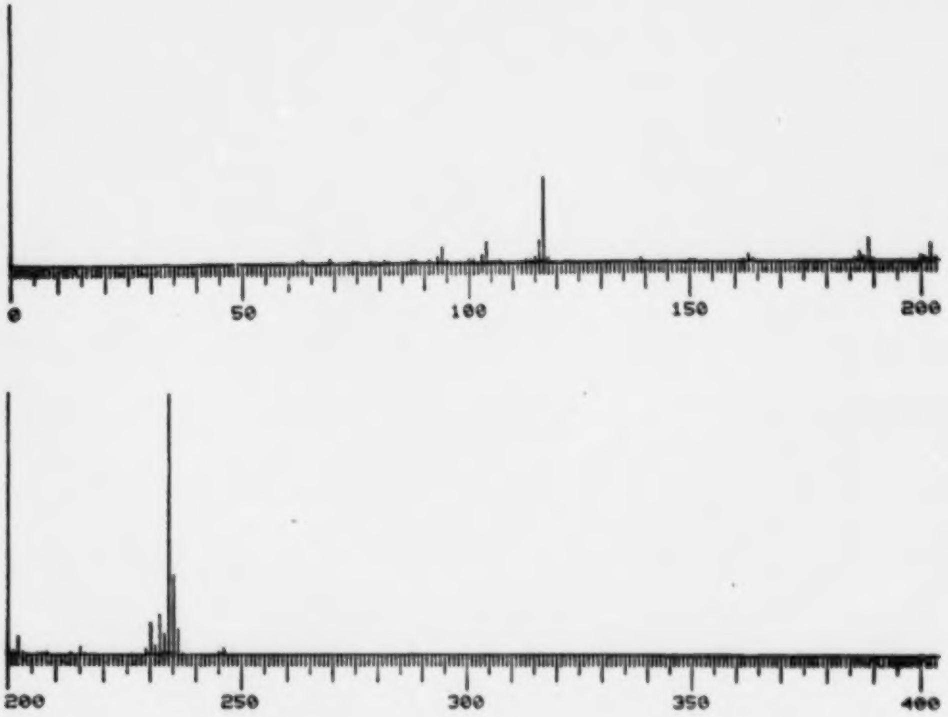


FIGURE 16

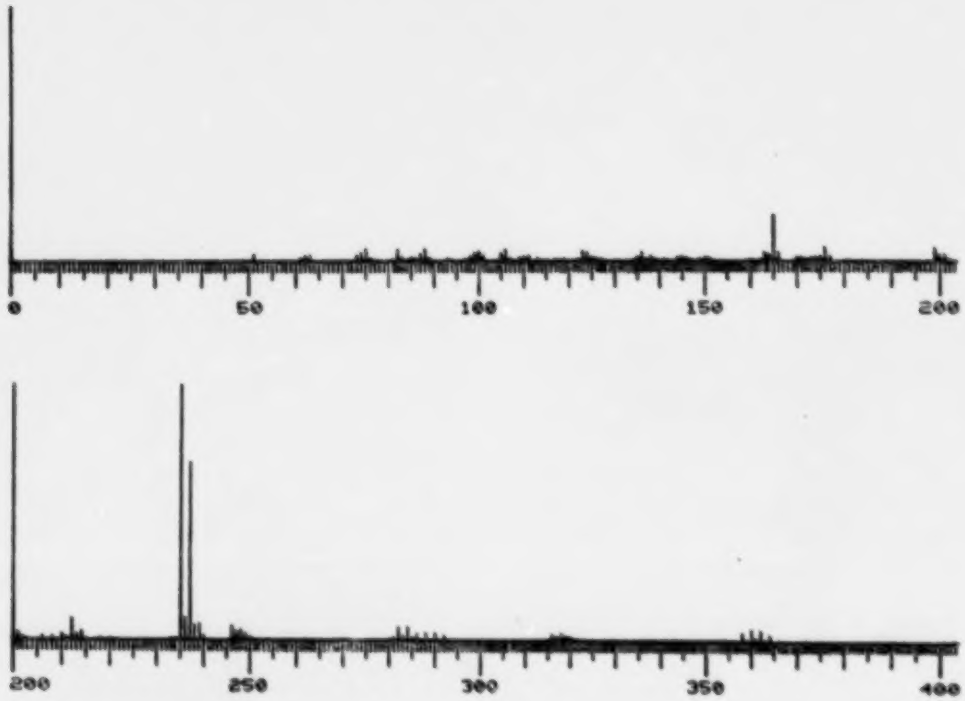
Mass spectrum of p,p'-DDT in sample 2-19-S.
In this sample, the identification is correct.

```
SEQUEN     28    PAGE      1

DRAW MS
GC ID EP    930   DATE    1/21/81
AQRATE        6   SCTIME       1   RESPWR    500
HIMASS      500   THRESH       1

2-19-S G32 + 5B

IGNORE     0,      0,      0,     0
%SCALE   100   #AMU'S   200      HRDCPY      NO
SUBTR      0   BASEPK     0      SCAN #     559
BKGRND   562
BASE    29263 *2** 2   % TOTAL IONIZ.      20
```



4. SEDIMENT SAMPLES

Of the three fractions that were derived (G31, G32, and G33), only the G32 fraction is discussed in detail. Examples of chromatograms from G31 fractions are presented in Appendix II. Since these fractions were judged to contain little information that could be correlated to toxic effects, no further effort was expended except to derive the chromatograms and store that information as raw data. Most G33 fractions contained only a few minor peaks and were not further pursued for this reason. Exceptions are noted in the text.

As mentioned before, the G32 fraction contains the majority of toxic compounds and, for this reason, most of the time available was expended in the analysis of this fraction.

A general overview of the presence of organic compounds in the Bay is presented in bar graphs; Figure 17a and 17b. In these figures, the sum of the concentrations in individual peaks of the chromatograms is represented by the length of the bar (on a logarithmic scale). The numbers on the vertical axis refer to station numbers whose position is found in the chart to the left.

Several interesting observations are immediately evident:

(a) The upper part of the Bay (north of the Patuxent River) contains organic compounds more uniformly distributed and generally at higher concentration than the lower part.

(b) Concentration sums of organic compounds present in lower Bay sediments tend to be higher at rivermouth stations (Lynnhaven, station 1; James, station 3; York, station 5; Rappahannock, station 8; Potomac, station 13; Patuxent, station 17) than in open Bay stations or in samples close to the Eastern Shore.

(c) In the upper Bay, samples collected at river mouths also tend to be high, but since in this area hydrocarbon levels are high in general, this feature is not obvious.

(d) Concentrations in sediments from the mouth of the Susquehanna River are indicated to be highly variable (it is relatively low in spring 1979, but very high in fall of the same year).

(e) Compared to other locations, seasonal variability is also indicated for a station southwest of Tilghman Island, which shows and unusually high concentration sums in fall 1979.

FIGURES 17-28: Station histograms for sediment samples collected during spring (a) or fall (b). The station locations and station numbers are indicated in the map. The vertical axis of the histograms contains the station numbers, the horizontal axis the concentrations on a logarithmic scale. Concentrations <10 ppb were omitted.

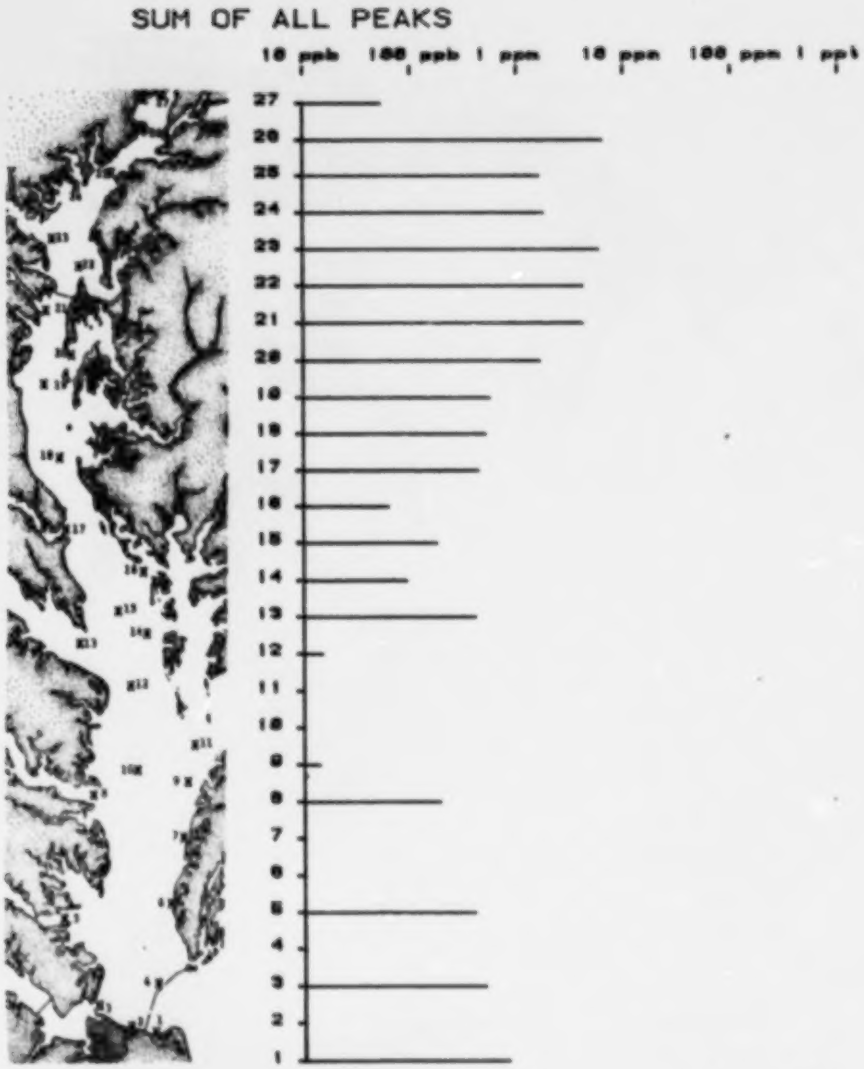
SUM OF ALL PEAKS
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 17a

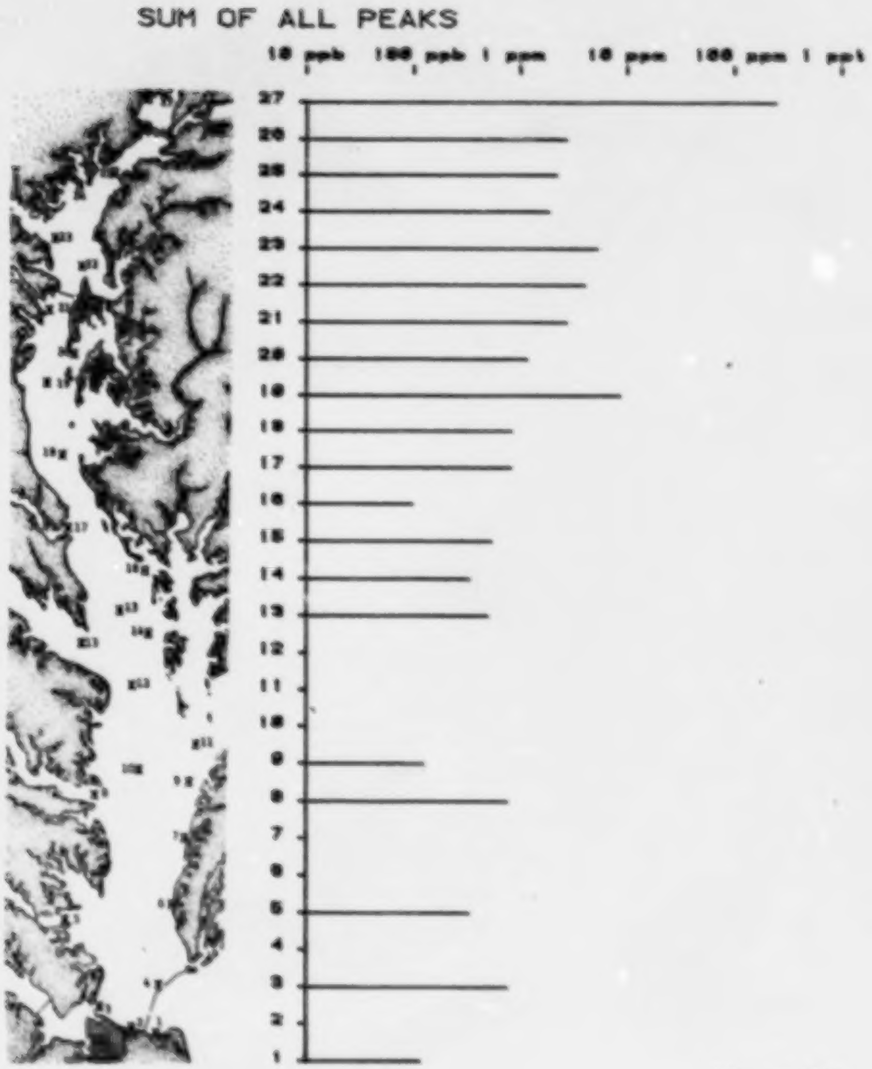

SUM OF ALL PEAKS
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 17b

While the concentration sums allow a judgement of the quantities of organic compounds encountered in the Bay, Figures 18a and 18b convey much more relevant information insofar as they now represent the concentration sums of a group of compounds that contains many toxic, carcinogenic, mutagenic and teratogenic members, the polynuclear aromatics or PNA's. All of the PNA's whose concentrations have been summed are unsubstituted and known to be generated in high temperature processes. As such, they are likely to be man-made pollutants (Youngblood and Blumer, 1975; Grimmer and Bohnke, 1972).

Although a "natural" origin in forest and prairie fires can be postulated (Youngblood and Blumer, 1975), their obvious preponderance in sediments near large population centers, industrial complexes and dense transportion networks (Baltimore, greater Norfolk area) or at the mouths of rivers that connect to such centres (James, Potomac, Susquehanna and Chesapeake-Delaware Canal) must be taken as evidence of man-made input.

All the trends that have been listed for Figures 17a and 17b generally also apply to the PNA's. Item (e) is a special case that will be discussed separately. Thus, statements (a)-(d) remain valid for PNA-sums, but "organic compounds" should now be replaced by "organic pollutants."

Bar graphs for major individual PNA's are found in Figures 19 to 27. They indicate that Baltimore Harbor, the Chesapeake-Delaware Canal and, in the fall 1979 sample, the Susquehanna River may be major sources of pollutants in sediments of the Chesapeake Bay.

A comparison of Figures 17 and 18 reveals that unsubstituted PNA's are the main pollutants contained in the sediment extracts. This is true throughout the Bay, except for station 2-19-S. Although many other compounds are present (see individual bar graphs at the different stations in Appendix III) and have been identified by GC-MS (Table 20), their concentration in general is low relative to those of unsubstituted PNAs. It is also interesting to note (Table 20) that fluorene and many substituted aromatic hydrocarbons such as napthalenes, biphenyls and acenapthenes are present, most of them very likely deriving from petroleum.

Other compound-types from EPA's priority pollutant list (EPA/NRDC, 1977) have been specifically sought but could not be found. This should not be interpreted that they are absent, but that their concentration relative to the hydrocarbons is so low they cannot be recognized in superimposed mass spectra.

In general, the complexity of upper Bay samples is formidable. Except for unsubstituted PNAs, there are few peaks in the high resolution chromatograms that represent one or two compounds only. More often, the mass spectra indicate the simultaneous presence of many compounds; while it is possible to separate and identify some of the more prominant components, others may not be recognizable.

The preponderance of hydrocarbons in the sediment samples did also manifest itself in a retention index-based search for chlorinated

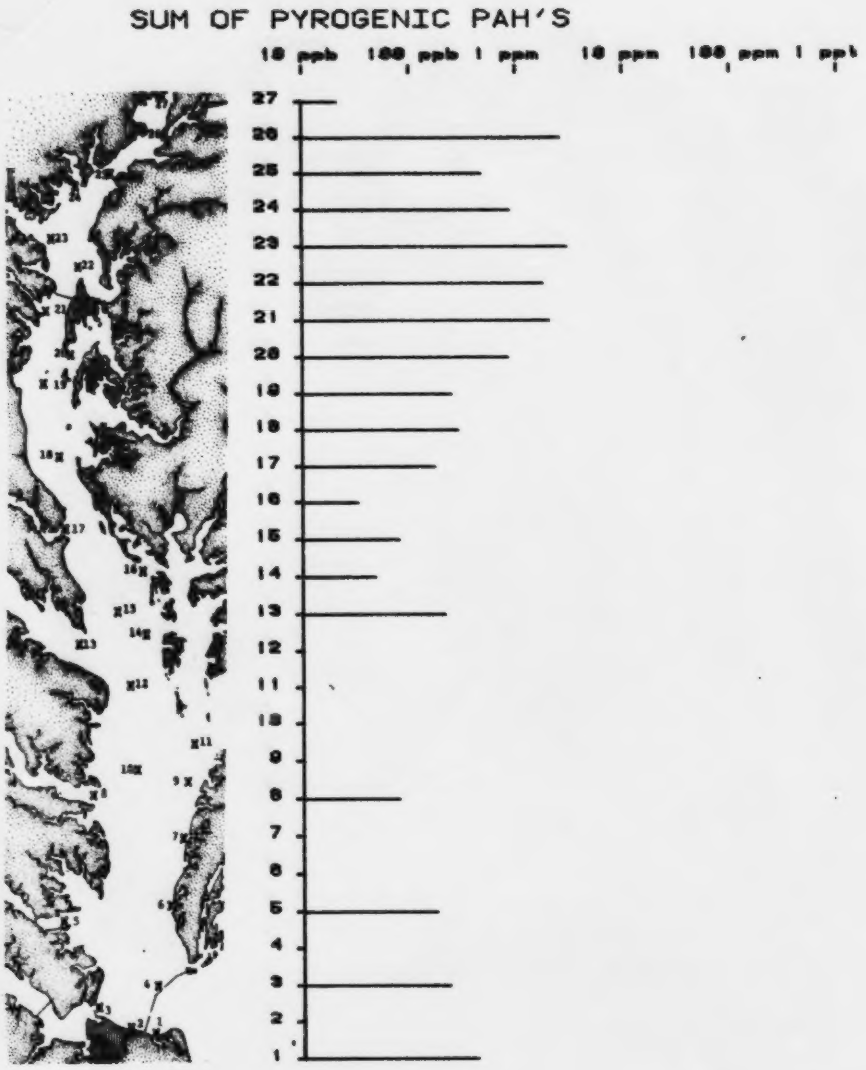

SUM OF PYROGENIC PAH'S
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 18a

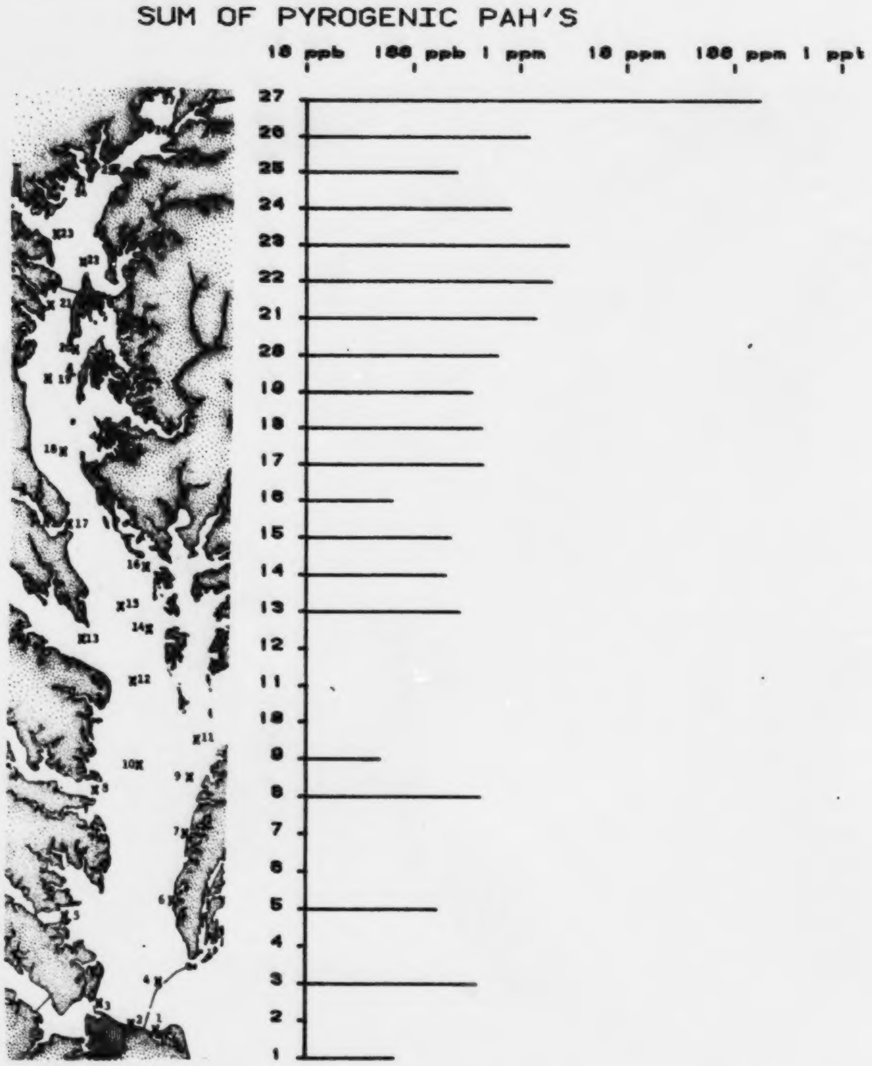

SUM OF PYROGENIC PAH'S
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 18b

ARI : 193.9 Dibenzothiophene

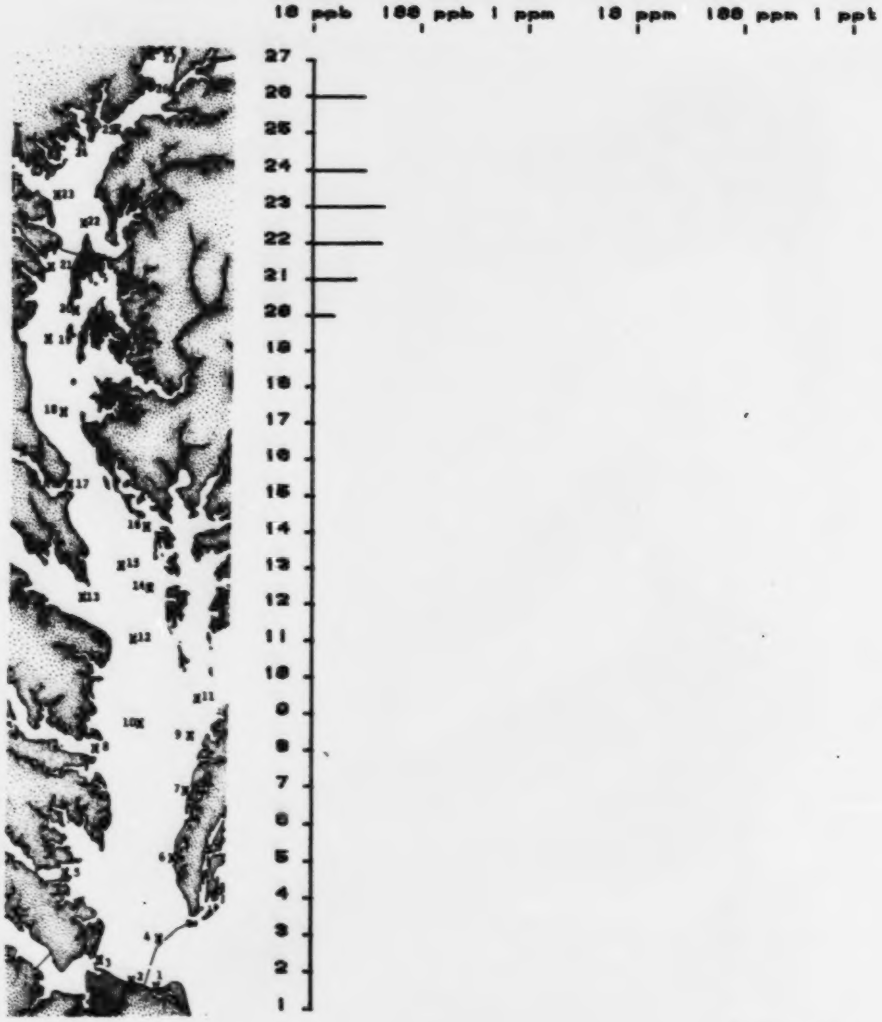


Figure 19a

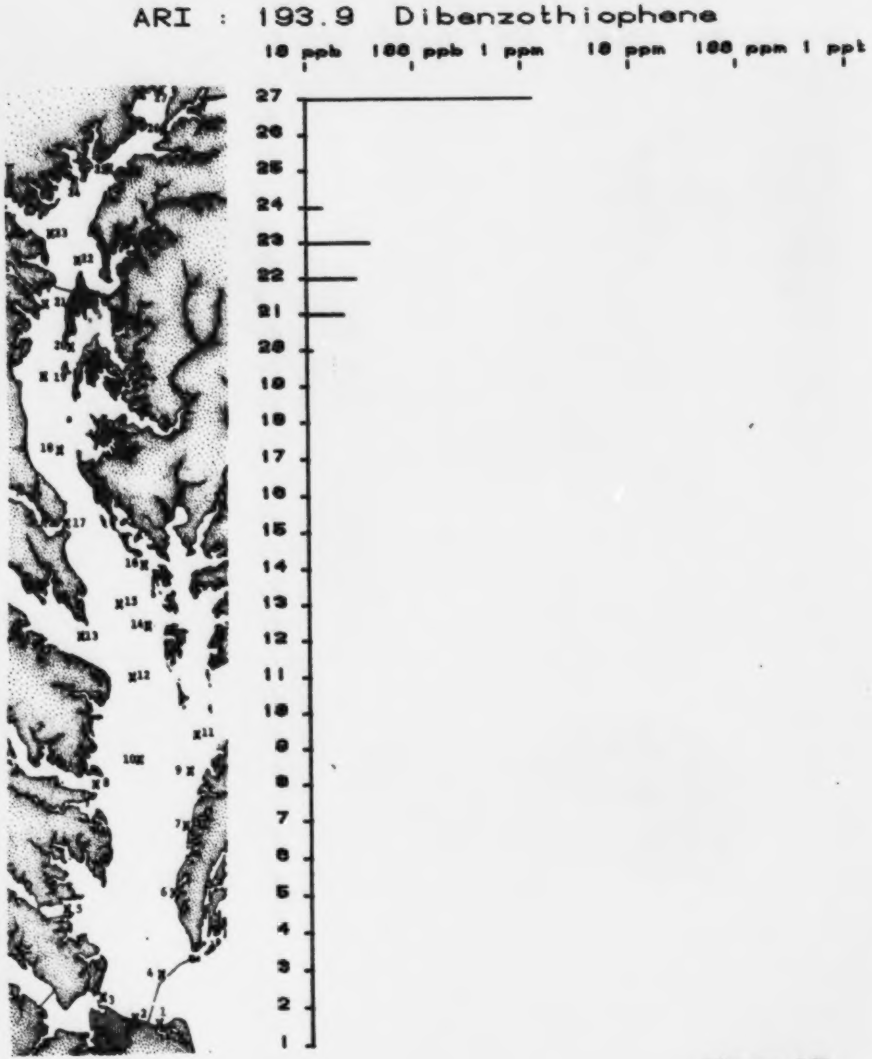

ARI : 193.9 Dibenzothiophene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 19b

ARI : 200 Phenanthrene

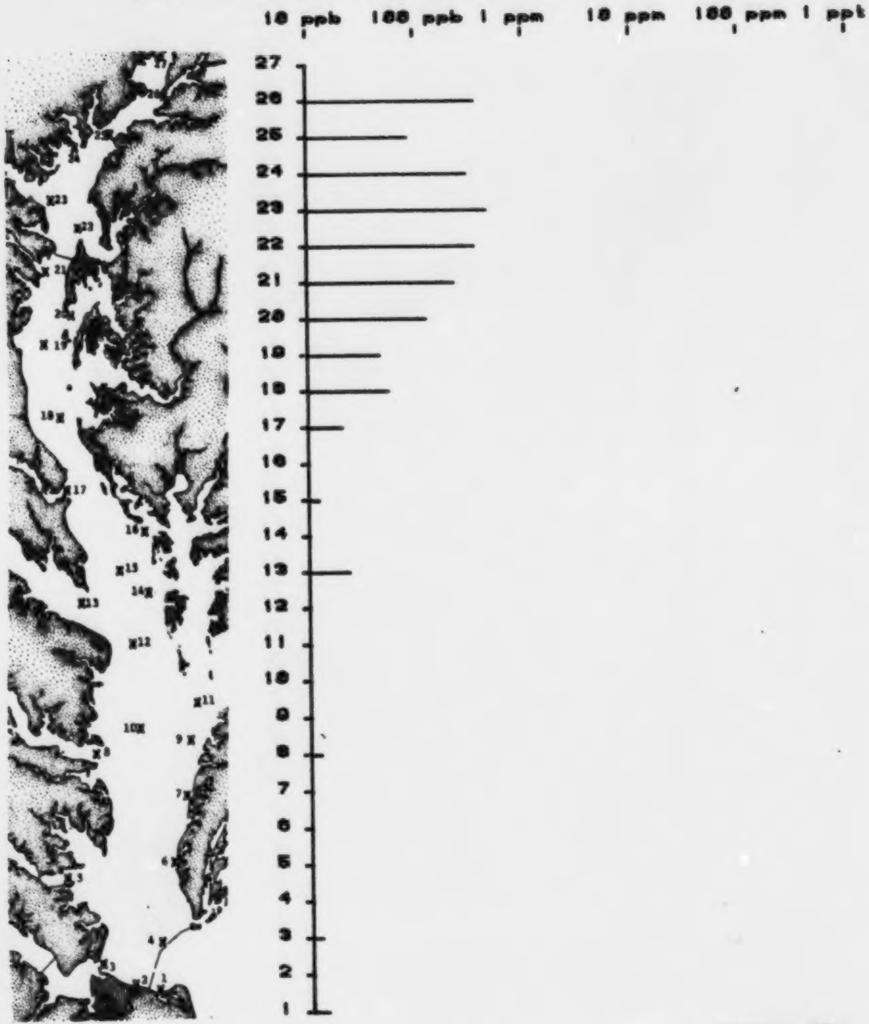


Figure 20a

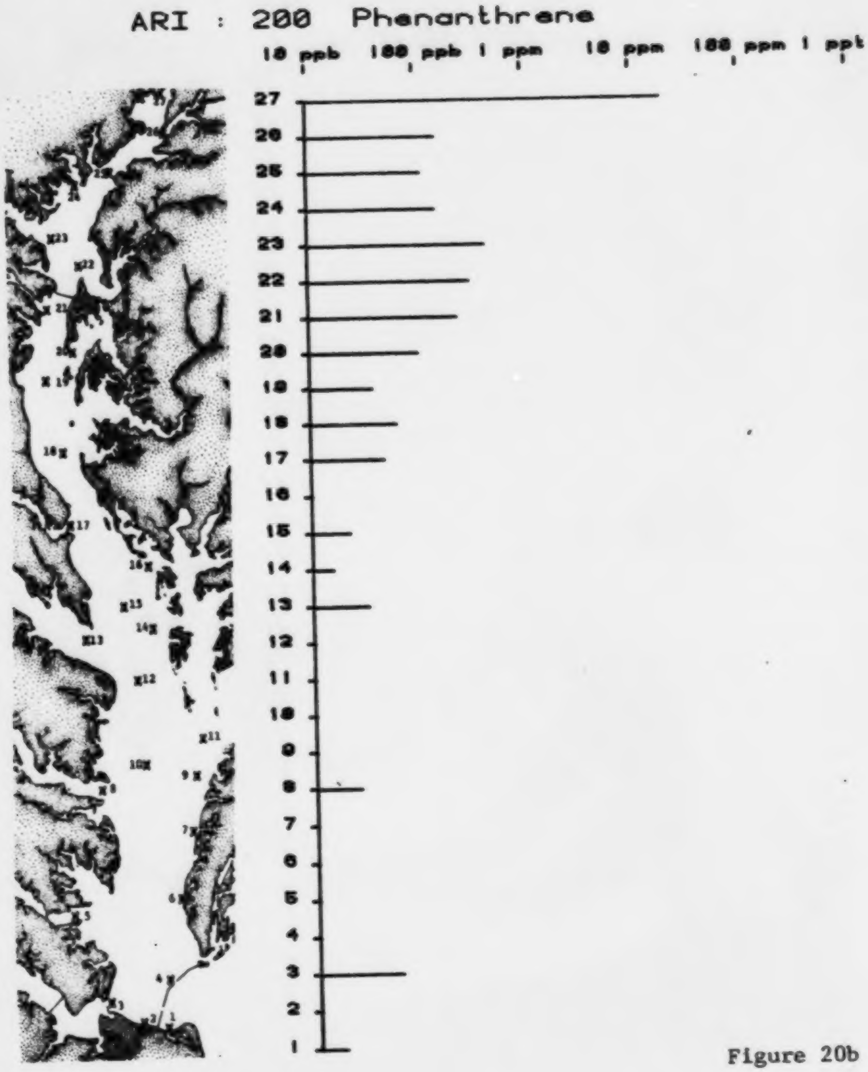

ARI : 200 Phenanthrene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 20b

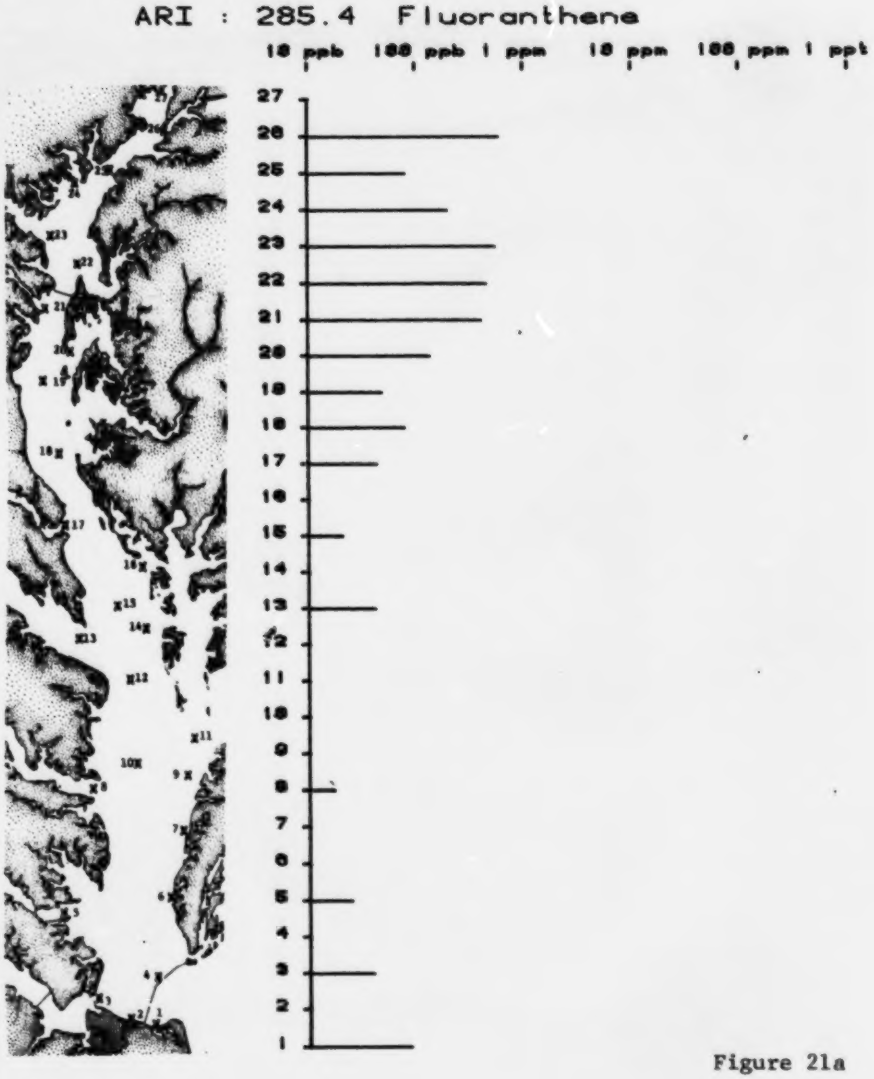

ARI : 285.4 Fluoranthene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 21a

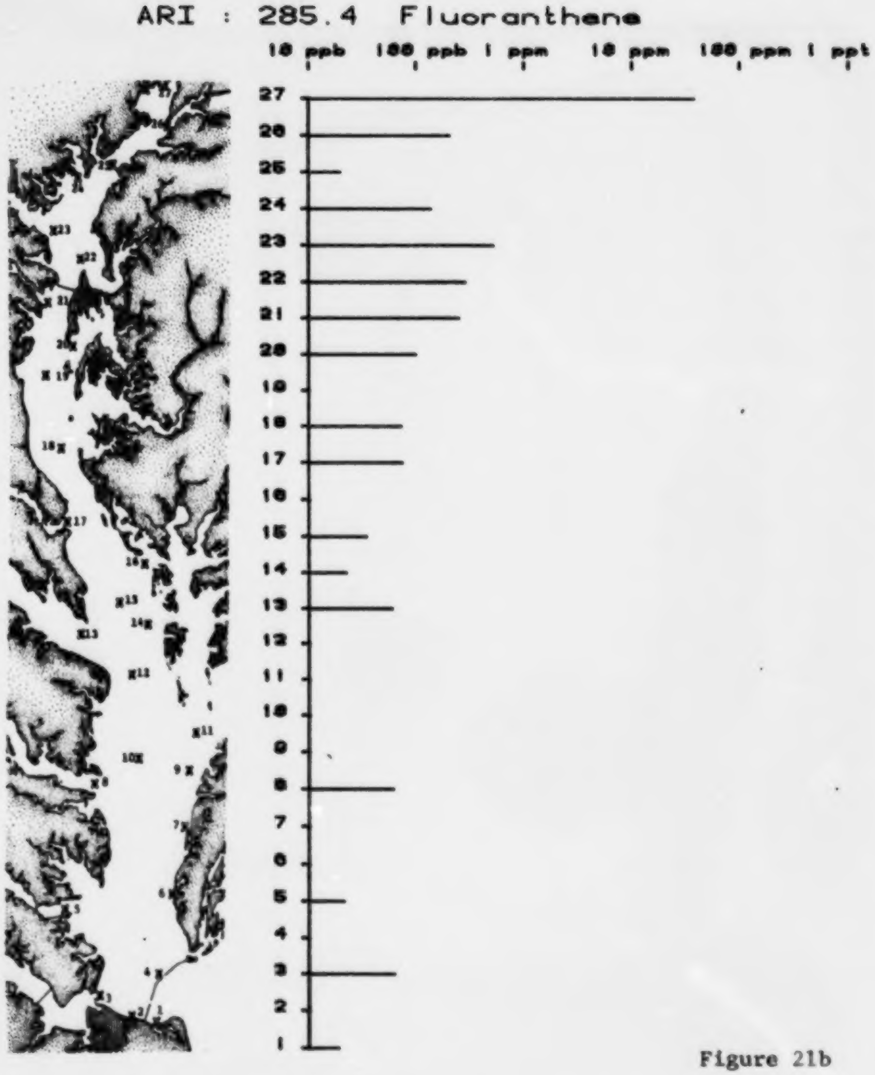

ARI : 285.4 Fluoranthene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 21b

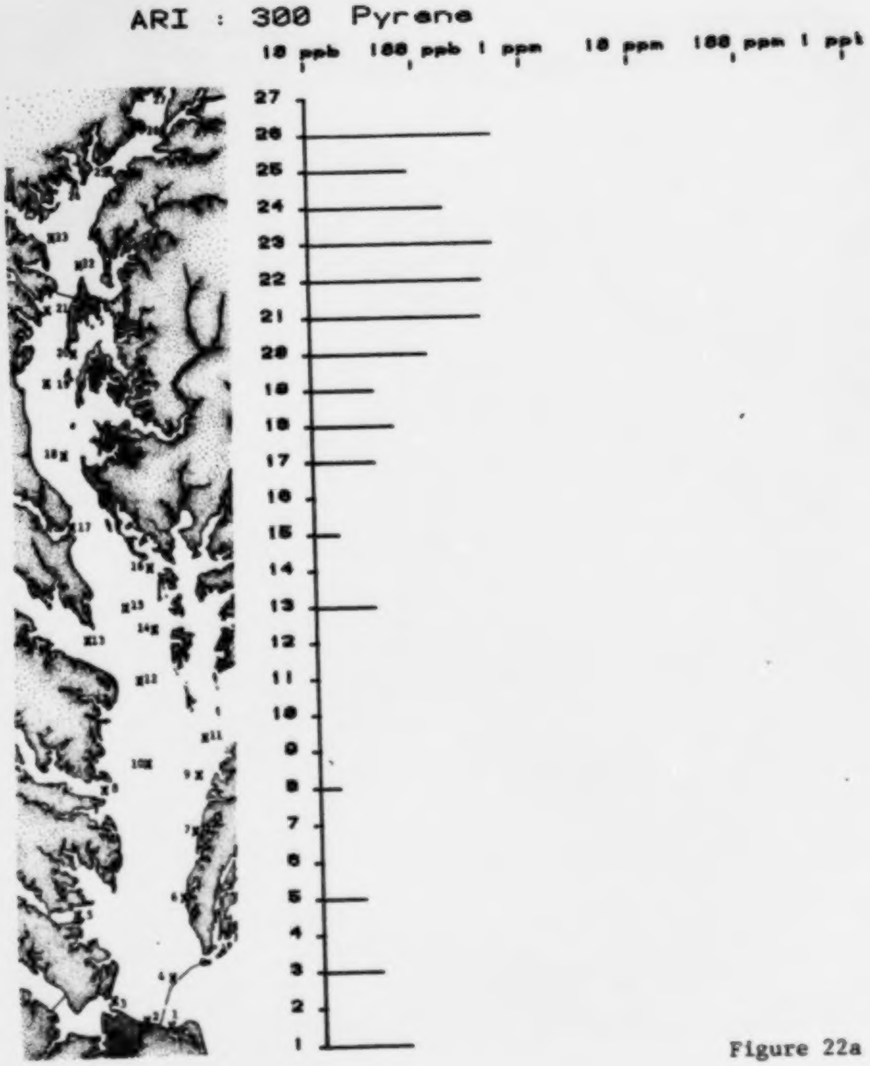
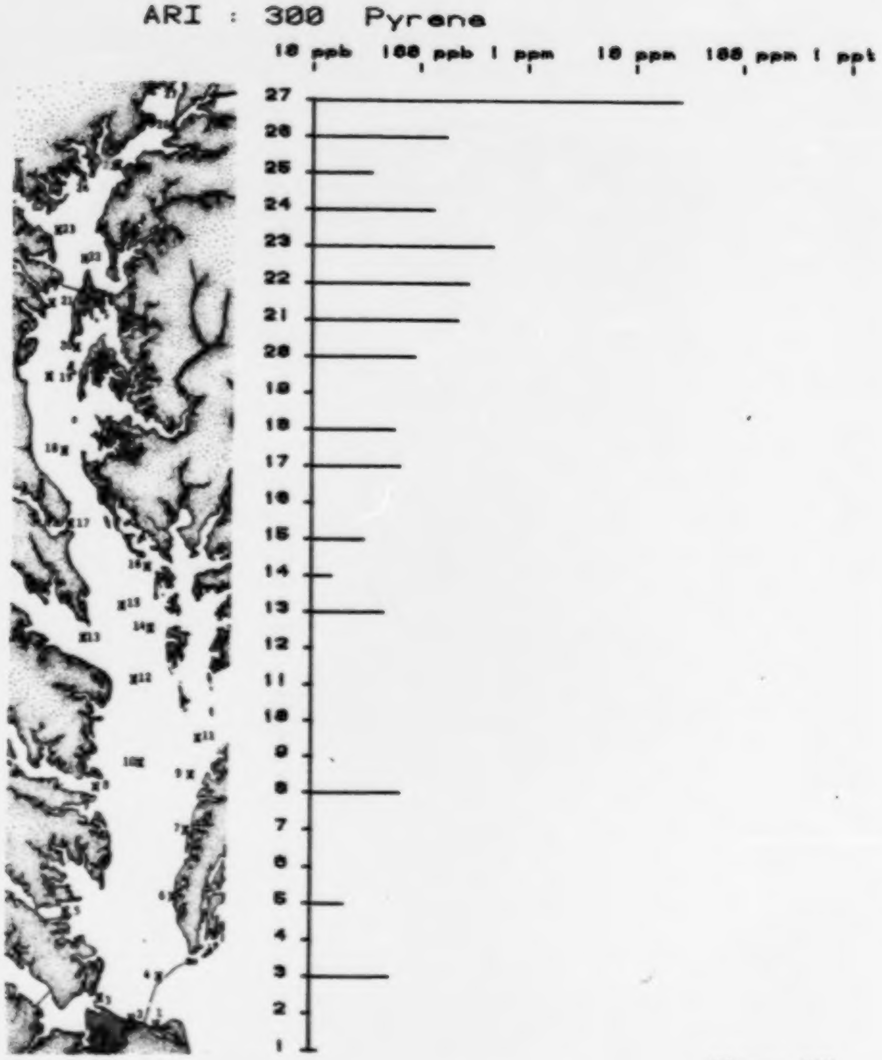

ARI : 300 Pyrene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 22a



ARI : 300 Pyrene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 22b

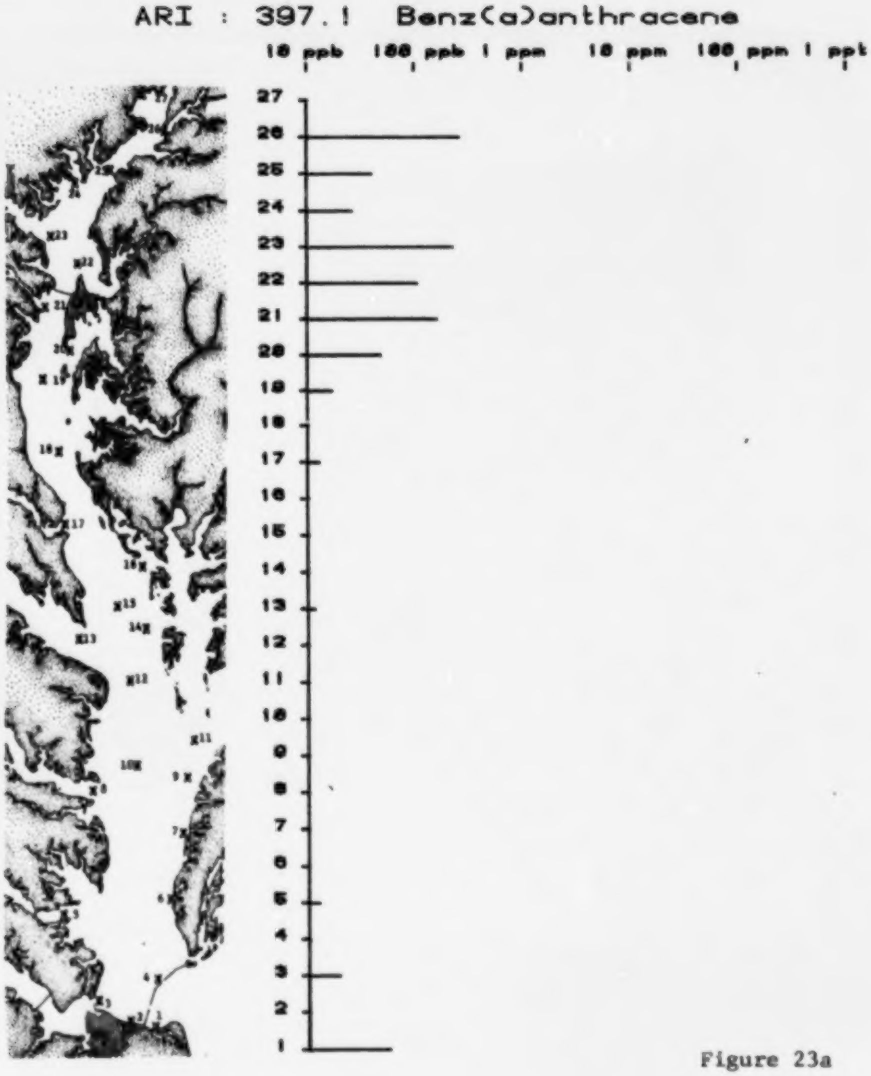

ARI : 397.1 Benz(a)anthracene
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 23a

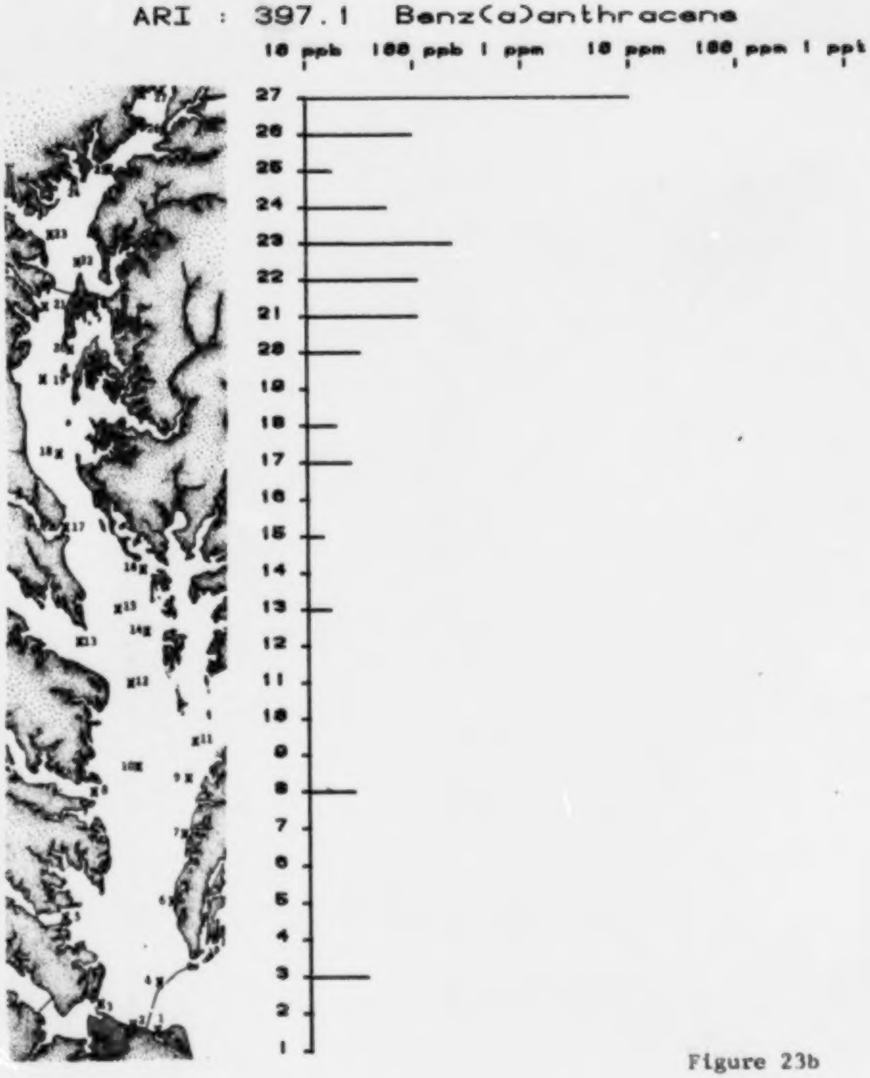


Figure 23b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin)
(4-75)

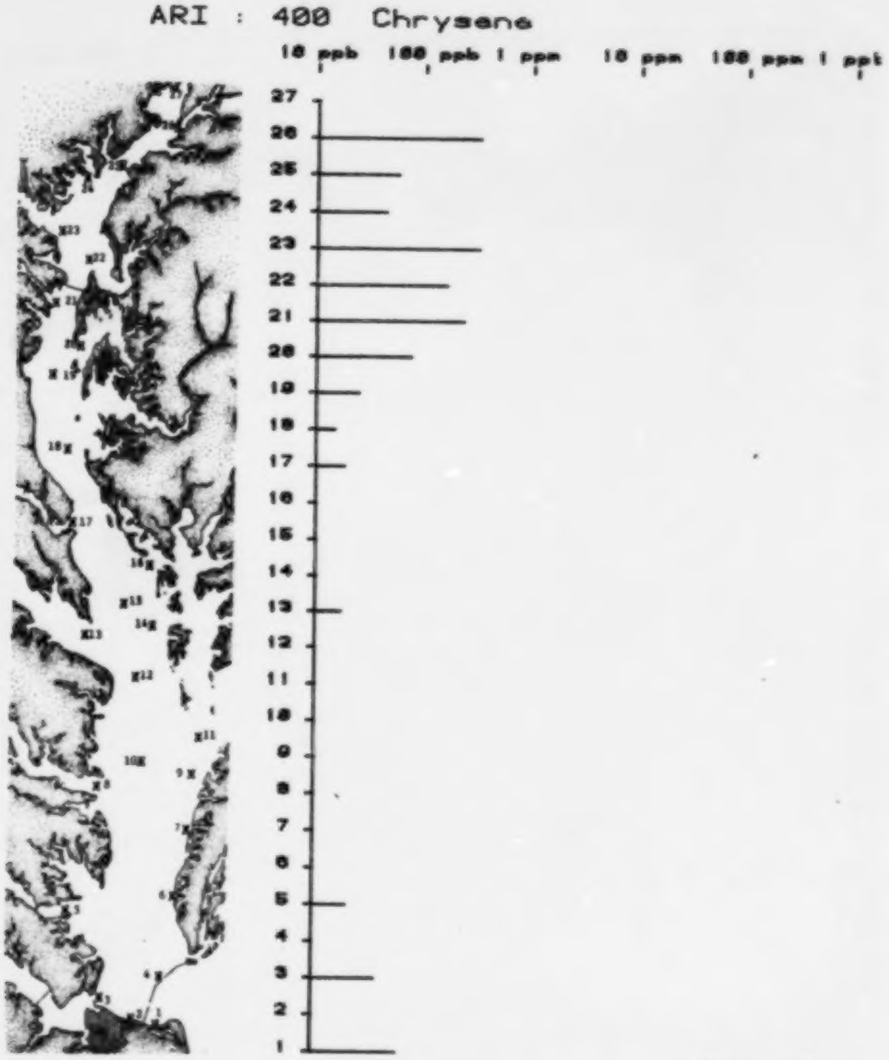


Figure 24a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.) (4-78)

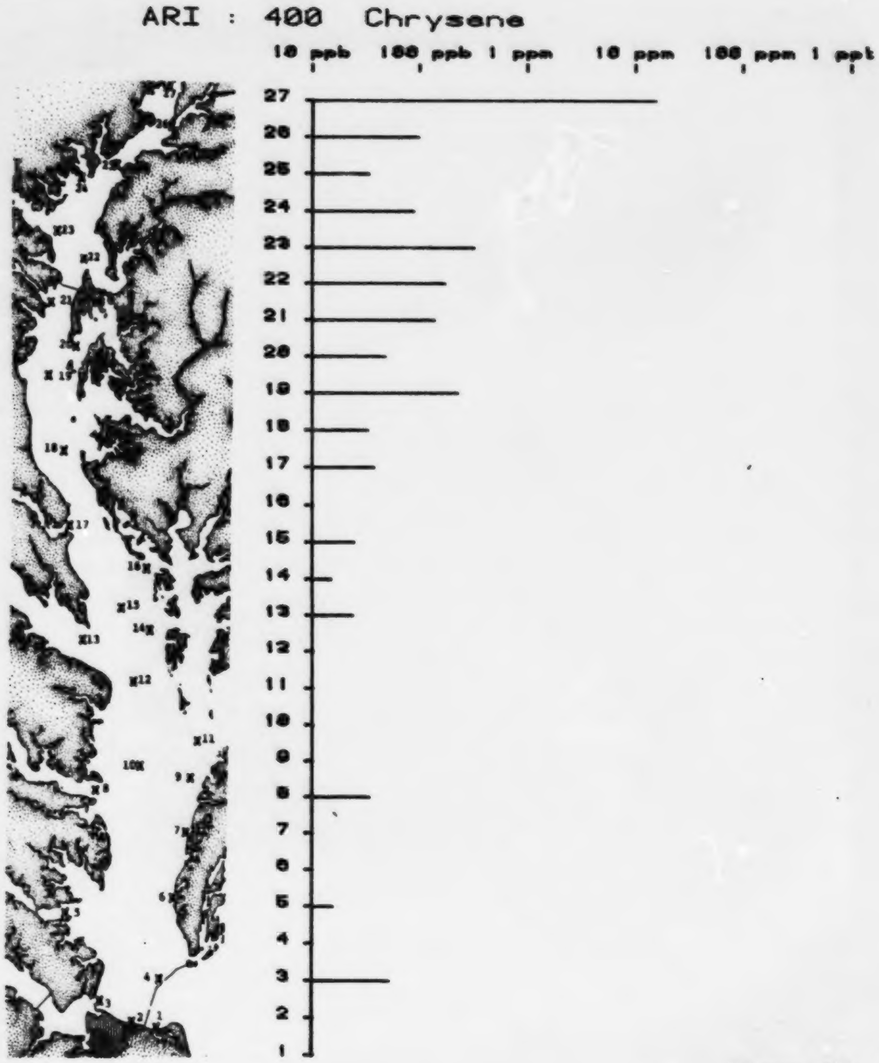


Figure 24b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

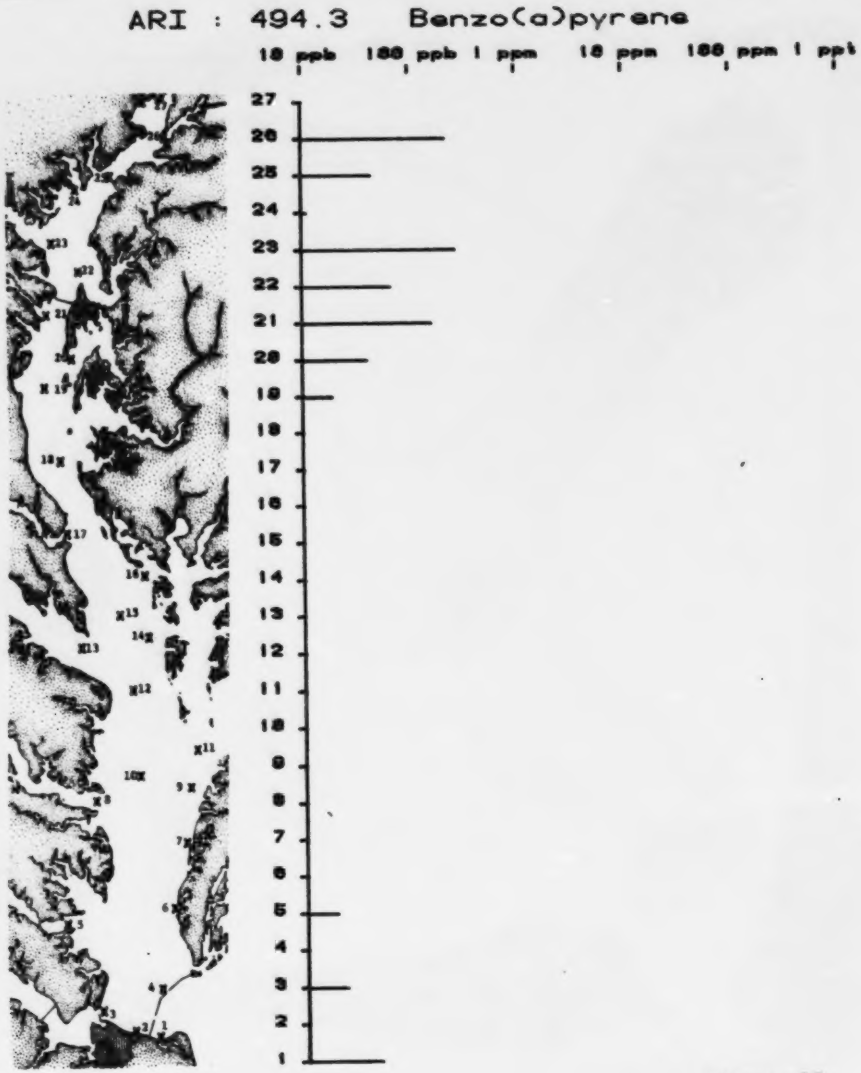


Figure 25a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

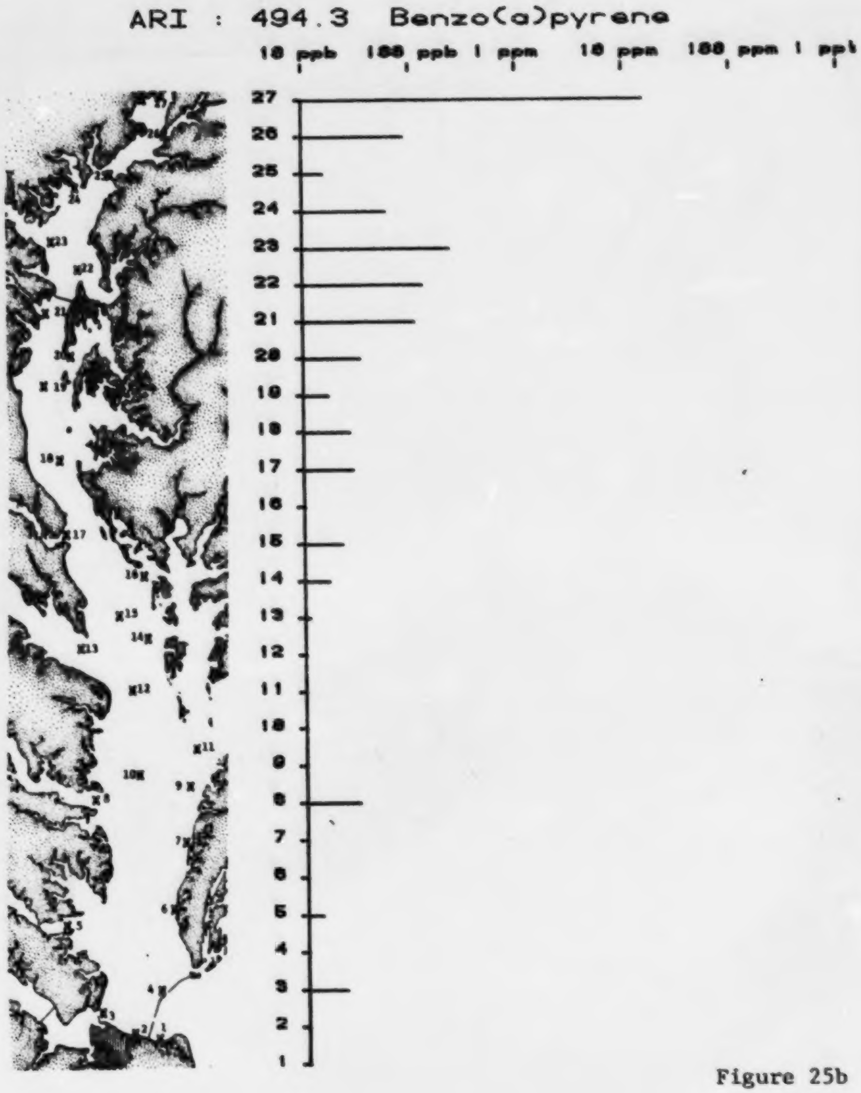


Figure 25b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

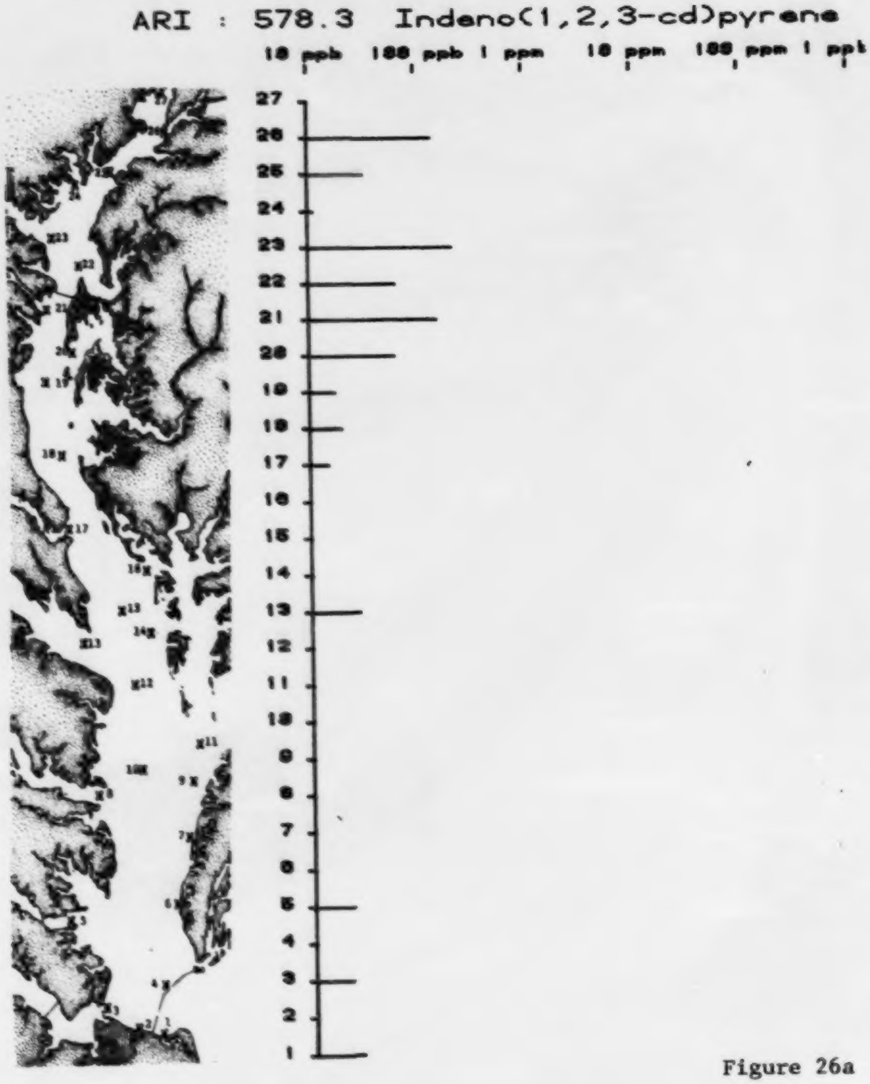


Figure 26a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

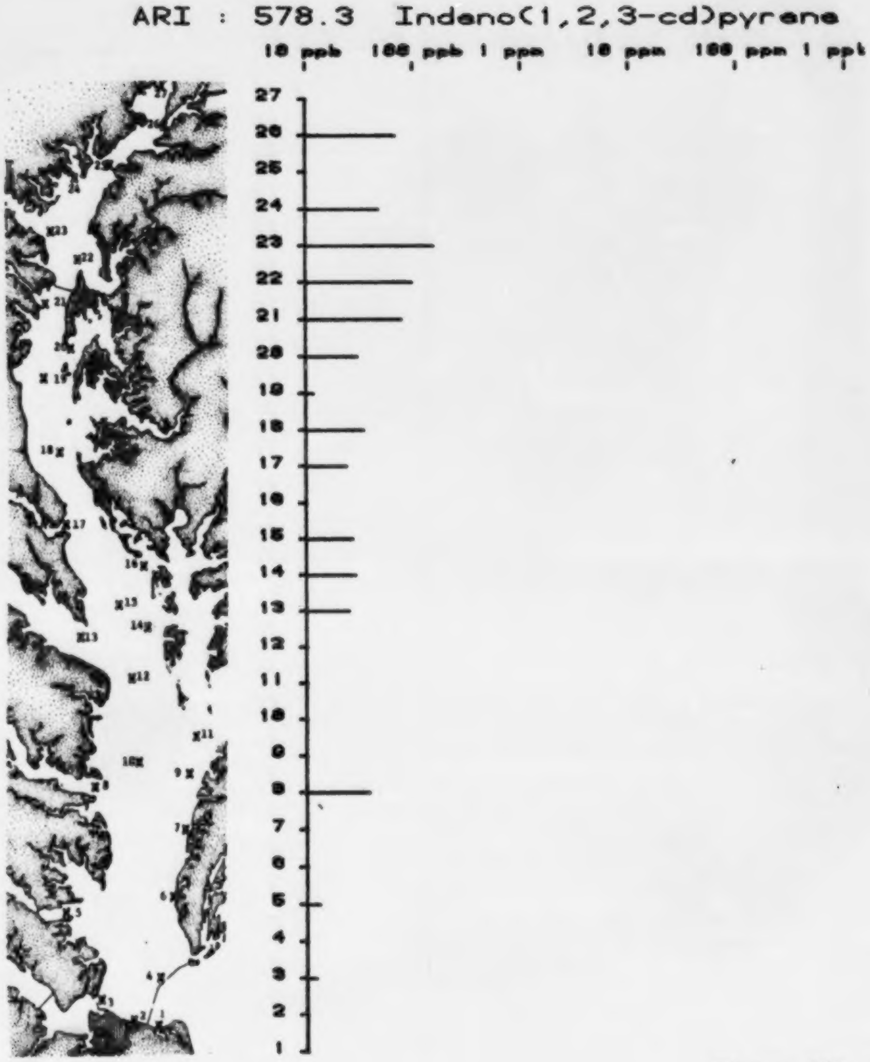


Figure 26b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

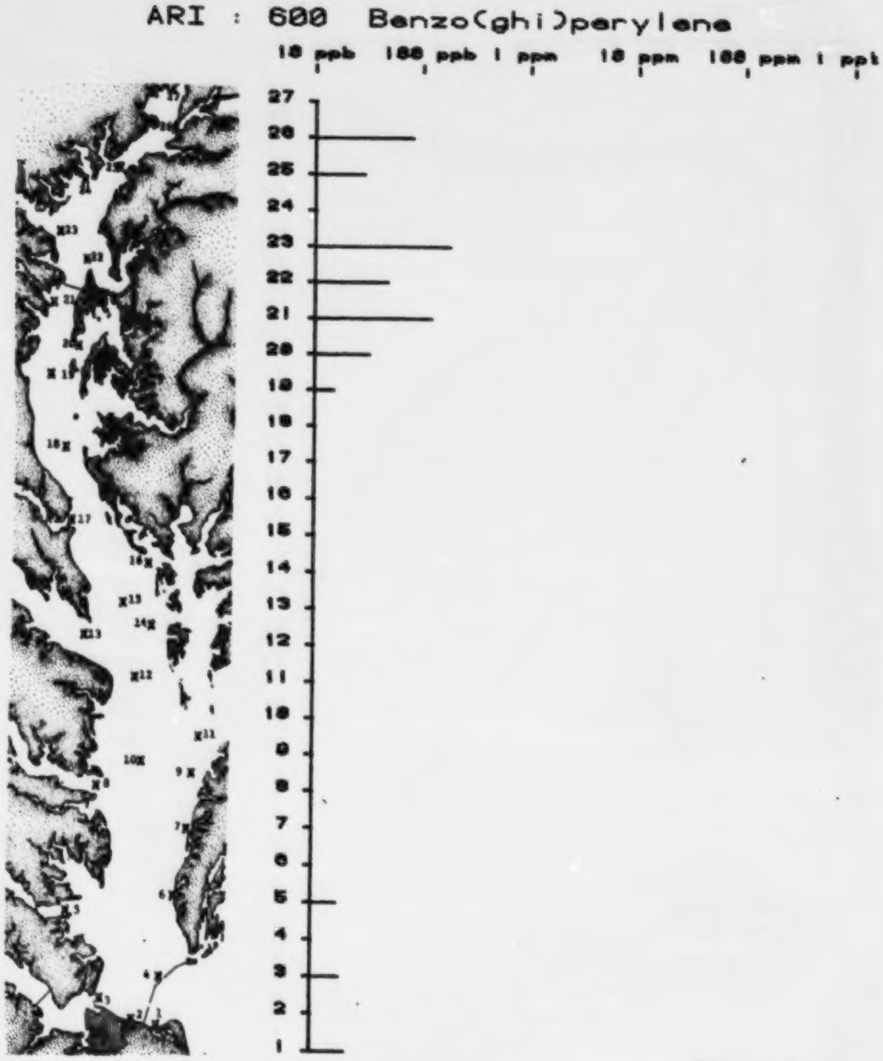


Figure 27a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

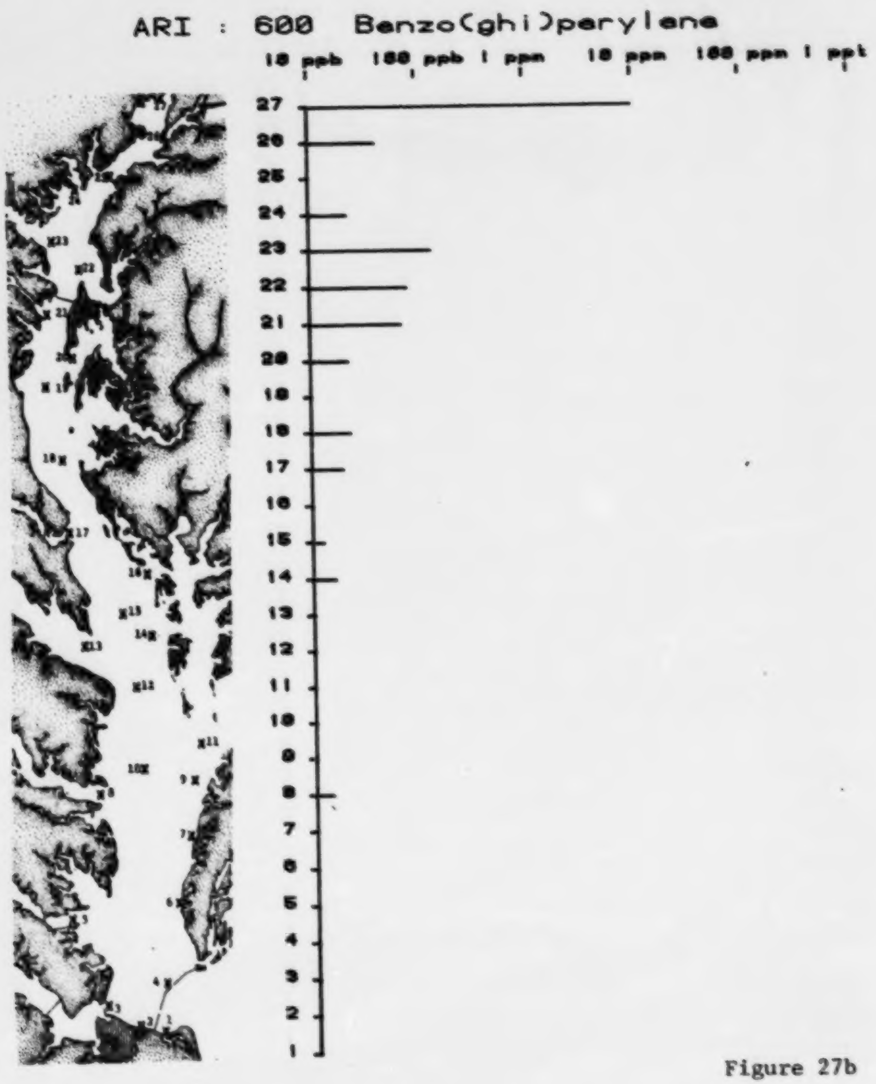


Figure 27b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

Table 20. Compounds identified by mass spectrometry - sediment samples. Numbers relate to position of peak in the chromatograms (in ARI units). Code: A - identified by comparison with reference spectrum[1,2]; A1 - by interpretation of mass spectrum; B - by mass spectrum and published ARI[3]; C - by mass spectrum and ARI established by standard in our laboratory; D - by mass spectrum and ARI extrapolated from crude oil sample.

Compound	Station									Code
	1-01-S	1-22-S	2-22-S	2-23-S	1-25-S	2-25-S	1-26-S	2-26-S	2-27-S	
Naphthalene	0	0	0	0	0	0	0	0	0	B,C
Benzothiophene	3.6	-	-	3.5	-	-	3.5	-	-	C
Benzothiazole	-	-	-	-	-	-	-	-	21.1	A
2-Me-Naphthalene	54.4	53.6	53.2	52.9	53.1	53.2	53.4	55.0	-	B,C
1-Me-Naphthalene	63.5	61.8	61.7	61.9	61.7	62.0	61.8	63.7	63.8	B,C
Unknown	?	-	92.7	-	-	-	-	-	-	
Biphenyl	100	100	100	100	100	100	100	100	100	B,C
Et-Naphthalene	-	103.5	103.5	103.4	-	103.5	103.7	103.4	-	B,D
C_2-Naphthalene	106.2	106.4	106.2	106.3	106.3	105.8	106.3	106.3	-	B,C
C_2-Naphthalene	-	-	109.9	-	-	-	-	-	-	B,D
C_2-Naphthalene	110.5	110.1	110.6	110.2	110.3	109.9	110.0	110.3	-	B,C
C_2-Naphthalene	-	-	-	110.9	-	-	-	111.1	-	B,D
1,4-Dihydro-1,4-Ethenonaphthalene	-	112.3	112.0	112.8	113.1	-	-	112.6	-	A
C_2-Naphthalene	-	114.7	114.7	115.2	114.9	114.6	114.8	115.3	-	B,C
Acenaphthylene	117.8	117.0	116.8	117.3	117.1	-	116.9	117.5	-	B,C
C_2-Naphthalene	-	118.8	118.7	119.4	-	118.7	118.9	119.3	-	B,D
Acenaphthene	127.5	126.1	126.2	126.8	126.3	125.7	126.3	127.0	127.0	B,C
4-Me-Biphenyl	-	127.6	127.6	128.4	128.6	127.5	127.8	128.3	-	B,D
3-Me-Biphenyl	-	129.9	129.7	130.6	-	129.8	129.9	130.5	-	B,C
C_3-Naphthalene	-	132.3	132.9	132.9	-	132.2	132.2	132.9	-	D
Dibenzofuran	135.4	134.1	134.3	135.1	134.9	134.5	134.4	135.1	135.2	B,C
C_3-Naphthalene	-	-	-	137.3	-	137.4	137.9	137.4	-	D
C_3-Naphthalene	-	137.7	137.7	138.5	138.3	138.6	138.9	138.5	-	D
C_3-Naphthalene	139.4	138.8	138.7	139.6	139.4	140.4	-	139.6	-	D
C_3-Naphthalene	144.3	143.3	143.4	144.4	144.0	143.3	143.6	144.3	-	D
Unknown	-	-	-	-	-	-	-	145.8	-	
C_3-Naphthalene	-	147.1	147.3	147.9	147.4	147.4	147.2	148.1	-	B,C
Me-Acenaphthylene	-	-	-	-	147.4	-	-	-	-	B
Me-Acenaphthylene	-	-	-	150.8	-	-	-	151.0	-	A1
C_3-Naphthalene	-	-	-	-	-	151.5	-	-	-	D
Fluorene	152.4	151.2	151.4	152.4	152.0	151.5	151.6	152.1	152.1	B,C
C_3-Naphthalene	-	152.8	153.1	153.9	-	153.2	-	153.5	-	D
Me-154	-	-	154.7	155.3	-	-	-	-	-	A1
C_2-154[4]	-	-	154.7	155.3	-	155.6	-	156.0	-	A1

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

Table 20 (continued).

Compound	Station 1-01-6	1-22-6	2-22-8	2-23-6	1-25-5	2-25-8	1-26-6	2-26-8	2-27-8	Code
2-Methylthio-Benzothiazole	-	156.5	156.4	157.4	-	157.3	157.9	157.2	-	C
C_3-Naphthalene	-	-	-	-	-	157.3	-	-	-	D
9-Me-Fluorene	-	-	-	-	-	157.3	-	-	-	B,D
Mixture	-	-	-	-	-	-	-	157.2	-	
C_2-Biphenyl	-	157.6	157.7	158.5	-	-	-	158.3	-	B
Mixture	-	159.4	160.0	160.8	-	-	-	-	-	
Unknown	-	161.7	162.2	162.4	162.3	-	161.9	162.7	-	
Me-Dibenzofuran/C_2-154	162.2	161.7	162.2	162.4	162.3	162.0	161.9	162.7	-	A1
Unknown	163.7	-	-	-	-	-	-	-	-	
Me-Dibenzofuran/C_2-154	165.4,	164.7	164.9	165.7	165.7	164.9	164.9	165.5	-	A1
Me-Dibenzofuran/C_2-154	-	167.1	-	-	168.0	167.3	167.4	167.9	-	A1
C_2-Biphenyl/C_2-Acenaphthene	-	-	167.3	168.0	-	-	-	-	-	A1
C_4-Naphthalene	-	167.1	-	-	-	-	-	-	-	D
C_4-Naphthalene	-	169.5	169.4	170.3	-	169.6	-	170.1	-	D
Unknown	-	-	170.7	171.2	-	170.8	-	-	-	
Unknown	171.1	-	-	172.4	-	171.9	-	171.2	-	
C_4-Naphthalene	-	174.6	174.7	175.2	-	174.9	174.7	175.2	-	D
Unknown	-	-	-	-	-	-	-	-	176.1	
C_4-Naphthalene	-	-	-	-	-	178.6	-	-	-	D
C_4-Naphthalene	-	-	178.9	179.2	-	179.5	179.0	179.3	-	D
Me-Fluorene	-	-	-	179.2	-	-	179.0	-	-	A1
2-Me-Fluorene	181.2	180.6	180.8	181.2	181.2	180.7	181.8	181.2	-	B
1-Me-Fluorene	182.6	182.4	182.4	182.6	182.9	182.5	182.6	182.6	182.5	B,C
C_2-Dibenzofuran	184.0	-	-	-	-	-	-	-	-	A1
Me-Fluorene	185.3	184.8	185.0	185.3	185.1	-	185.3	185.1	-	D
C_4-Naphthalene	-	-	-	-	-	185.4	-	-	-	A1
C_2-Dibenzofuran/C_3-154	190.6	190.1	-	190.2	-	190.1	-	190.1	-	A1
9-Fluorenone	-	190.1	190.1	190.2	190.3	-	190.2	190.1	-	B
C_4-Naphthalene	-	-	-	-	-	190.1	-	-	-	A1
C_2-Dibenzofuran/C_3-154	-	191.1	-	-	192.0	191.2	191.5	191.4	-	A1
C_2-Dibenzofuran/C_3-154	193.8	-	-	-	-	-	-	193.3	-	A1
Dibenzothiophene	193.8	193.0	193.2	193.1	193.1	193.0	193.3	193.3	193.1	B,C
C_2-Dibenzofuran/C_3-154	195.4	-	194.3	194.5	-	194.7	194.7	194.2	-	A1
Me-Fluorene	-	-	194.3	-	-	-	-	-	-	A1
C_2-Dibenzofuran/C_3-154	-	-	196.9	196.8	-	-	-	197.5	-	A1
Phenanthrene	200	200	200	200	200	200	200	200	200	B,C
Anthracene	203	202.5	202.9	202.2	203.2	203.2	203.0	202.5	202.4	B,C
C_2-Dibenzofuran/C_3-154	-	-	-	-	-	203.2	-	-	-	A1

Table 20 (continued).

Compound	Station									Code
	1-01-8	1-22-8	2-22-8	2-23-8	1-25-8	2-25-8	1-26-8	2-26-8	2-27-8	
C_2-Dibenzofuran/C_3-154	-	-	-	-	-	204.0	-	-	-	A1
Mixture	206.2	207.5	207.3	207.5	-	207.2	208.1	208.0	207.1	
C_2-Fluorene	211.7	212.1	212.3	212.1	212.8	212.0	212.9	212.1	-	D
C_2-Fluorene	214.2	214.3	214.3	214.3	215.2	215.2	214.8	214.3	-	D
C_2-Fluorene	215.7	216.0	216.3	216.2	216.8	216.8	216.6	216.5	-	D
Chlorinated compound	-	-	-	-	-	-	216.6	-	-	
Mixture	-	-	-	-	-	218.4	-	-	-	
C_2-Fluorene	220.0	220.7	221.1	220.3	-	220.0	221.1	220.6	-	D
Me-Dibenzothiophene	223.6	223.0	223.2	223.9	223.4	223.3	223.7	223.2	222.7	D
C_2-Dibenzofuran/C_3-154	-	-	-	-	-	223.3	-	-	-	A1
C_3-Fluorene	-	-	226.7	226.4	-	-	-	-	-	A1
C_3-Dibenzofuran/C_4-154	226.0	-	-	226.4	-	225.6	227.2	226.8	-	A1
1,4-Dihydro-1,4-Ethanoanthracene	226.0	226.5	226.7	226.4	-	-	227.2	226.8	226.5	A
C_3-Dibenzofuran/C_4-154	-	-	-	-	-	228.0	-	-	-	A1
1-Phenylnaphthalene	-	-	-	-	-	228.0	-	-	-	B,C
Me-Dibenzothiophene	229.9	229.4	230.0	229.7	230.4	230.4	230.1	229.6	-	D
3-Methyl Phenanthrene	236.2	236.9	236.8	236.8	236.8	236.8	236.9	236.6	236.2	B
2-Methyl Phenanthrene	237.7	238.2	237.8	238.3	238.4	238.4	238.5	238.1	237.7	B
2-Methyl Anthracene	240.9	-	-	-	-	-	-	240.7	-	B,C
4-H-Cyclopenta(def)phenanthrene	242.9	242.6	242.5	242.4	242.4	242.4	243.0	242.3	241.8	C
Me-Phenanthrene	243.7	244.2	244.0	244.0	244.8	244.0	244.4	243.8	-	B
1-Methyl Phenanthrene	245.4	-	245.0	245.4	-	245.6	245.7	245.2	244.8	B,C
Me-Phenanthrene	-	-	-	248.5	-	-	-	-	-	
C_3-Fluorene	-	-	-	-	-	-	249.1	248.4	-	D
Me-Phenylnaphthalene	251.9	-	-	-	-	-	-	-	-	A1
C_2-Dibenzothiophene	251.9	252.1	252.9	252.7	-	-	253.0	252.5	-	A1
C_2-Dibenzothiophene	254.3	254.3	254.7	254.3	255.2	-	255.2	254.8	-	D
C_3-Fluorene	255.4	-	-	-	-	256.8	-	-	-	A1
2-Phenylnaphthalene	259.6	260.8	260.9	260.8	261.6	261.6	261.3	261.3	260.2	B,C
Anthraquinone	259.4	260.8	260.9	260.8	261.6	-	-	-	-	C
C_3-Dibenzothiophene	259.6	260.8	260.9	260.8	261.6	261.6	261.3	261.3	-	D
C_3-Dibenzothiophene	-	-	266.2	-	-	-	-	-	-	D
C_2-Phenanthrene	265.2	-	-	265.5	266.4	266.4	-	-	-	A1
C_2-Dibenzothiophene	268.0	268.8	268.7	268.4	268.8	269.6	-	-	-	D
C_3-Fluorene	-	-	-	-	-	269.6	-	-	-	A1
Bis(4-Chlorophenyl)-Methanone	-	268.8	270.0	269.3	-	-	269.5	269.8	-	C
C_2-Phenanthrene	270.2	271.2	-	270.8	272.0	272.0	271.1	272.3	-	B,C
C_2-Phenanthrene	273.3	273.5	-	273.4	274.4	274.6	274.0	274.2	-	B,D

Table 20 (continued).

Compound	1-01-S	1-22-S	2-22-S	2-23-S	1-25-S	2-25-S	1-26-S	2-26-S	2-27-S	Code
	Station									
C_3-Dibenzothiophene	-	-	-	-	-	-	-	276.2	-	Al
Elemental Sulfur	276.0	-	276.1	-	-	276.4	-	-	-	A
C_2-Phenanthrene	276.0	-	276.1	-	-	-	-	277.1	-	B,D
C_2-Phenanthrene	278.1	278.7	279.5	278.7	279.2	279.2	279.3	278.8	278.6	D
Me-4H-Cyclopentaphenanthrene	-	-	-	-	-	-	-	-	278.6	Al
C_2-Phenanthrene	-	-	-	280.6	-	280.8	280.8	-	-	D
C_2-Phenanthrene	281.8	-	-	281.6	-	282.4	283.0	282.3	-	D
C_3-Dibenzothiophene	-	-	-	-	-	-	283.0	-	-	Al
Me-4H-Cyclopentaphenanthrene	-	-	-	281.6	-	-	-	-	-	Al
C_2-Phenanthrene	-	-	-	-	283.2	-	-	-	-	Al
C_2-Phenanthrene	-	-	-	-	-	285.6	-	-	-	D
Fluoranthene	285.6	285.6	285.7	285.7	285.6	285.6	285.9	285.7	285.7	B,C
C_3-Dibenzothiophene	288.1	289.0	289.4	288.8	289.6	289.6	289.5	289.0	-	D
C_2-Phenanthrene	288.1	289.0	289.4	288.8	289.6	289.6	289.5	289.0	-	D
Acephenanthylene	-	292.2	292.4	291.6	292.8	-	292.4	292.1	-	Al
Me-Phenylnaphthalene	292.6	-	-	-	-	-	-	-	-	D
Me-Phenylnaphthalene	295.1	294.0	294.3	293.9	295.2	294.4	294.7	293.9	294.1	Al
Benzo(def)Dibenzothiophene	295.1	294.0	294.3	293.9	295.2	294.4	294.7	293.9	294.1	B
Me-Phenylnaphthalene	-	-	296.4	296.3	297.6	296.8	296.9	296.1	-	Al
C_3-Dibenzothiophene	-	-	296.4	-	-	-	-	-	-	Al
Pyrene	300	300	300	300	300	300	300	300	300	B,C
Me-Phenylnaphthalene	302.5	302.7	303.1	302.7	303.4	303.4	303.4	302.8	302.5	Al
C_3-Dibenzothiophene	-	302.7	303.1	302.7	-	-	-	302.8	-	D
Me-4H-Cyclopentaphenanthrene	-	302.7	303.1	302.7	303.4	303.4	303.4	302.8	302.5	Al
C_3-Phenanthrene	-	305.2	305.6	305.2	-	-	-	305.1	-	D
Me-Phenylnaphthalene	307.6	307.6	308.0	307.9	308.6	308.6	308.5	308.2	307.4	Al
C_3-Dibenzothiophene	-	307.6	308.0	307.9	308.6	308.6	308.5	308.2	-	Al
C_3-Phenanthrene	-	-	-	-	-	308.6	-	-	-	Al
Me-Phenylnaphthalene	312.7	312.7	312.5	312.5	313.8	-	313.2	312.4	312.1	Al
C_3-Phenanthrene	-	312.7	312.5	-	313.8	312.9	-	312.4	-	D
C_3-Phenanthrene	-	314.0	314.4	313.9	315.5	314.7	314.9	314.0	-	D
Unknown	-	314.0	314.4	313.9	-	-	314.9	314.0	-	
C_3-Phenanthrene	-	-	-	317.8	-	-	318.4	-	-	D
C_3-Phenanthrene	-	319.3	319.6	319.3	319.0	319.8	-	319.3	-	D
Me-Phenylnaphthalene	318.8	319.3	319.6	319.3	319.0	-	-	319.3	318.6	Al
Me-Phenylnaphthalene	-	-	-	320.7	-	-	320.2	-	-	Al
C_3-Phenanthrene	-	-	-	320.7	-	-	320.2	-	-	D
Me-202	321.3	321.6	321.9	321.6	322.4	322.4	322.3	321.8	320.5	Al

Table 20 (continued).

Compound	Station									Code
	1-01-S	1-22-S	2-22-S	2-23-S	1-25-S	2-25-S	1-26-S	2-26-S	2-27-S	
C_3-Phenanthrene	-	325.6	325.8	325.8	-	-	326.1	325.3	-	D
C_2-Phenylnaphthalene	-	325.6	325.8	-	-	-	-	-	-	A1
p,p'-DDE	-	-	-	325.8	-	-	326.1	325.3	-	C
Chlorinated compound	-	328.1	-	-	-	-	-	-	-	
Me-202	-	328.1	-	-	-	-	-	327.8	-	A1
Me-202	329.8	329.9	330.1	329.7	328.4	329.3	330.5	329.1	329.7	A1
C_2-Phenylnaphthalene	-	329.9	-	-	-	-	-	-	-	A1
C_3-Phenanthrene	-	-	-	-	328.4	329.3	-	-	-	D
C_3-Phenanthrene	-	-	-	-	-	331.0	-	-	-	D
Benzo(a)fluorene/Me-202	-	-	-	-	331.0	331.0	-	-	-	B,C
C_3-Phenanthrene	-	-	-	-	-	333.4	-	-	-	A1
9,10-Diethylphenanthrene	-	333.5	333.6	333.2	334.5	333.4	333.8	333.1	-	B
Me-202	335.1	-	-	-	-	-	-	-	-	A1
Benzo(b)fluorene/Me-pyrene	336.3	336.2	336.1	336.0	337.1	337.1	336.0	336.1	335.0	B,C
Me-Phenylnaphthalene	339.6	339.7	-	340.7	340.5	-	-	341.4	338.3	A1
C_2-Phenylnaphthalene	339.6	339.7	340.6	340.7	-	-	-	-	-	A1
Me-Phenylnaphthalene	-	-	-	341.3	-	-	-	-	-	A1
C_2-Phenylnaphthalene	-	-	-	341.3	-	-	-	-	-	A1
Me-202	343.2	342.9	343.2	342.9	344.0	-	343.6	343.5	342.3	A1
C_2-Phenylnaphthalene	-	-	-	-	-	343.1	-	-	-	A1
C_2-Phenylnaphthalene	345.2	-	345.2	345.2	-	345.7	345.5	-	344.4	A1
1-Me-Pyrene	345.2	345.0	345.2	345.2	345.7	345.7	345.5	345.4	344.4	B
Me-202	-	-	-	347.8	-	-	348.1	-	348.3	A1
C_2-Phenylnaphthalene	-	-	-	-	-	-	-	-	348.3	A1
Unknown	-	-	-	347.8	-	-	-	-	-	
Mixture	349.6	350.1	351.1	350.5	-	351.7	351.5	350.7	349.7	
Mixture	-	-	352.3	-	352.6	-	-	-	-	
C_2-202	-	-	-	-	-	-	-	-	354.1	A1
C_2-202	357.1	357.4	358.5	357	358.6	-	358.4	-	-	A1
C_4-Phenanthrene	357.1	-	358.5	-	-	-	-	-	-	D
C_3-202	-	-	358.5	-	358.6	-	-	-	-	A1
Unknown	360.0	-	-	360.1	-	-	-	-	359.4	
Chlorinated compound	-	-	-	360.1	-	-	-	-	-	A1
Unknown	-	-	-	-	-	-	-	-	364.4	
C_2-202	365.0	365.8	365.6	365.5	366.4	366.4	366.5	366.0	-	A1
C_3-Phenylnaphthalene	365.0	-	-	-	-	-	366.5	-	-	A1
C_2-202	370.6	371.1	371.1	370.9	371.6	371.6	371.6	371.4	370.1	A1
C_3-Phenylnaphthalene	370.6	-	-	-	-	-	-	-	-	A1

Table 20 (continued).

Compound	Station 1-01-8	1-22-8	2-22-8	2-23-8	1-25-8	2-25-8	1-26-8	2-26-8	2-27-8	**Code**
C_3-202	-	-	-	-	-	-	-	-	370.1	A1
C_2-202	-	-	-	-	-	-	373.6	372.8	-	A1
C_2-202	-	-	377.1	376.8	-	-	-	-	-	A1
C_3-Phenylnaphthalene	-	-	377.1	-	-	377.6	-	-	-	A1
Benzo(b)naphtho(2,1-d)thiophene	377.2	377.3	377.1	376.8	377.6	377.6	377.8	377.3	376.1	B
Benzo(ghi)fluoranthene	380.3	380.2	380.2	379.8	380.2	-	380.3	380.7	379.0	B
Benzo(c)phenanthrene	380.3	-	-	379.8	-	-	381.5	380.7	379.8	B
C_2-202	-	380.2	-	379.8	-	-	-	-	-	A1
C_2-202	-	-	-	-	381.0	381.0	-	-	-	A1
Benzonaphthothiophene	384.5	-	384.6	384.2	384.5	-	384.7	-	383.2	A1
Benzoacridine	-	384.1	-	-	384.5	-	384.7	384.0	383.2	B
C_2-202	-	-	384.6	384.2	-	-	-	385.3	-	A1
C_2-Phenylnaphthalene	-	-	-	-	-	-	-	-	384.3	A1
C_2-202	386.2	-	-	-	-	386.2	387.3	-	-	A1
C_3-Phenylnaphthalene	386.2	-	-	386.9	-	-	-	-	-	A1
Me-Benzofluorene/C_2-202	-	-	387.1	-	-	-	-	387.1	-	A1
Me-Benzophenanthrene	386.2	-	-	-	-	-	-	-	-	A1
Unknown	-	-	-	-	-	-	-	387.1	-	
Benzonaphthothiophene	390.9	390.1	391.1	390.5	390.5	-	390.8	390.5	389.5	A1
Unknown	-	-	-	-	-	-	-	390.5	-	
Cyclopenta(cd)pyrene	-	393.8	-	393.4	-	-	394.5	394.1	-	B
C_2-202	-	-	-	393.4	-	-	-	-	-	A1
Unknown	-	-	-	-	392.2	-	-	-	-	
Unknown	-	-	-	-	-	-	394.5	-	-	
Benzo(a)anthracene	396.8	397.2	397.0	396.9	396.6	397.4	397.5	397.1	396.5	B,C
Chrysene/Triphenylene	400	400	400	400	400	400	400	400	400	B,C
Unknown	404.4	404.2	404.2	404.4	-	-	404.4	-	403.9	A1
Me-228	-	-	-	404.4	-	-	-	-	-	A1
Unknown	-	-	-	-	404.0	-	-	403.6	-	
Me-Benzonaphthothiophene	-	-	406.1	405.7	-	-	-	-	-	A1
C_4-202	-	-	406.1	-	-	-	406.2	-	-	A1
Phenylphenanthrene	-	407.2	-	407.4	407.4	-	-	-	406.6	A1
Me-228	-	-	-	-	-	-	-	-	406.6	A1
Phthalate	-	-	407.9	-	-	-	-	-	-	A1
Unknown	-	-	-	-	408.1	-	408.2	407.4	-	
1,2'-Binaphthyl	-	-	-	-	408.1	-	408.2	-	409.5	B
C_4-202	-	-	-	-	-	-	-	409.1	-	A1
Me-Benzonaphthothiophene	-	412.0	412.2	412.0	411.3	-	412.6	-	-	A1
Me-228	412.6	-	412.2	412.0	-	-	412.6	-	411.4	A1

BEGIN LAST LINE OF TEXT
3/4"
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
DROPPED HEAD; BEGIN SECTIONS HERE
CENTER OF PAGE
TOP OF IMAGE AREA
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER

Table 20 (continued).

Compound	Station 1-01-6	1-22-6	2-22-6	2-23-6	1-25-6	2-25-6	1-26-6	2-26-6	2-27-6	Code
Me-228	414.1	414.3	-	414.3	-	-	-	414.7	414.7	A1
C_4-202	-	414.3	-	414.3	-	-	-	414.7	414.7	A1
9-Phenylphenanthrene	-	414.3	-	-	-	-	-	414.7	-	B
Mixture	-	-	416.4	-	414.5	-	414.9	-	-	
Me-226	-	-	-	-	-	-	-	-	415.8	A1
Me-Benzonaphthothiophene	419.1	418.7	419.0	418.8	418.5	-	419.3	419.0	-	A1
Me-228	419.1	418.7	419.0	418.8	-	-	-	419.0	418.2	A1
C_4-202	-	-	-	-	-	-	-	-	418.2	A1
Me-Benzonaphthothiophene	-	424.5	424.9	423.5	-	-	-	-	422.9	A1
Me-228	423.2	424.5	424.9	423.5	-	-	-	-	422.9	A1
Phthalate	423.2	-	-	-	-	-	-	-	-	A1
Me-Benzonaphthothiophene	-	-	-	424.7	-	-	-	424.6	-	A1
Me-228	-	-	-	424.7	425.1	-	-	424.6	-	A1
Phthalate	-	-	-	-	-	-	-	-	426.5	A1
Me-228	426.5	427.2	426.9	426.7	426.6	-	427.3	426.6	-	A1
Me-228	429.4	429.6	429.9	429.8	429.0	429.6	429.9	429.6	428.5	A1
Phthalate	-	-	-	-	429.0	-	-	-	-	A1
Me-228	432.1	432.3	432.4	432.2	-	432.0	432.3	432.1	431.2	A1
C_2-228	-	-	-	-	-	-	-	-	431.2	A1
Me-226	434.8	434.8	-	-	-	-	-	434.8	433.5	A1
Me-228	434.8	-	-	-	435.5	-	-	-	-	A1
Me-228	-	436.4	436.4	436.5	-	-	-	-	-	A1
Me-226	436.8	436.4	436.4	436.5	-	-	436.7	436.2	435.9	A1
Me-226	438.8	-	-	438.4	-	-	438.6	-	437.6	A1
Me-228	-	438.6	438.6	438.4	437.9	-	-	438.3	437.6	A1
C_2-226/1-Phenylphenanthrene	-	438.6	438.6	-	-	-	-	438.3	437.6	B
Unknown	-	-	-	-	440.3	-	-	-	-	
2,2'-Binaphthyl	-	-	-	-	-	-	-	-	442.5	B
Unknown	444.5	444.9	445.1	444.8	444.4	444.8	445.5	444.8	-	
Unknown	447.1	447.2	447.3	447.4	-	-	-	-	446.6	
Mixture	451.2	450.4	450.5	449.9	-	-	449.8	448.2	-	
Mixture	454.6	454.1	454.4	454.5	-	-	-	-	-	
Chlorinated compound	-	454.1	-	-	-	-	-	452.7	-	A1
Unknown	-	-	-	-	-	-	-	-	453.4	
Unknown	-	-	-	-	-	-	-	-	456.6	
C_2-228	458.6	457.7	458.7	458.2	457.3	-	458.1	457.8	-	A1
C_2-228	-	-	-	-	-	-	-	460.8	-	A1
C_2-228	463.6	463.6	463.0	463.4	462.9	-	463.8	463.2	-	A1
C_2-226	-	-	-	463.4	-	-	-	-	-	A1

Table 20 (continued).

Compound	Station									Code
	1-01-S	1-22-S	2-22-S	2-23-S	1-25-S	2-25-S	1-26-S	2-26-S	2-27-S	
C_2-228	467.4	466.2	465.9	466.5	465.3	-	466.8	466.1	467.0	A1
C_2-228	-	-	-	-	-	470.4	-	469.9	-	A1
Me-254	-	-	-	470.3	-	-	-	-	-	A1
C_4-202	-	-	-	-	470.2	-	-	-	-	A1
Unknown	-	-	-	-	-	470.4	-	-	-	
C_2-226	-	-	-	-	-	-	-	469.9	-	A1
Benzo(j,b,k)fluoranthenes	475.4	475.4	474.1	475.3	473.4	472.0	474.1	474.2	476.8	B,C
Benzo(e)acephenanthrylene	481.6	480.3	480.9	480.8	479.0	479.2	480.6	480.3	480.7	A1
C_4-220	-	483.3	-	483.3	485.5	-	-	483.1	483.3	A1
C_2-228	-	-	-	-	-	-	-	-	483.3	A1
Unknown	-	-	-	-	-	-	-	-	483.3	
Chlorinated compound	-	-	-	-	-	-	-	485.8	-	A1
Benzo(e)pyrene	491.6	490.6	490.4	491.0	488.7	488.8	490.7	490.2	492.3	B,C
Benzo(a)pyrene	494.9	494.1	493.3	494.3	491.7	491.2	493.2	493.5	495.9	B,C
Perylene	500	500	500	500	500	500	500	500	500	B,C
Me-252	505.7	505.6	505.0	505.4	505.4	-	505.2	505.1	505.6	A1
Me-252	-	508.8	508.8	508.7	-	-	-	509.4	508.9	A1
Terpenoid	-	-	-	-	-	-	509.2	509.4	-	A1
Me-252	-	-	-	-	512.0	-	-	-	-	A1
Me-252	513.7	514.4	515.3	515.4	514.1	-	-	-	514.4	A1
Unknown	-	-	515.3	-	-	-	-	-	514.4	
Me-252	516.0	517.0	-	-	516.3	-	516.2	516.1	-	A1
Unknown	-	-	-	-	516.3	-	-	-	-	
Me-252	-	-	-	-	520.7	-	-	519.1	-	A1
Hopanoid	-	-	-	-	-	-	-	519.1	-	A1
Me-252	522.9	522.4	522.7	522.8	-	-	522.7	522.4	522.4	A1
Me-252	-	523.9	-	524.0	-	-	524.2	-	-	A1
Unknown	-	-	-	524.0	-	-	-	-	-	
Me-252	-	-	527.6	528.5	-	-	-	528.7	527.7	A1
Me-252	529.8	529.6	529.9	-	530.4	530.4	530.0	-	-	A1
Unknown	533.1	533.0	532.5	533.0	-	-	533.0	532.3	531.3	
Me-252	-	-	-	-	-	-	533.0	532.3	-	A1
Me-252	-	535.8	536.3	536.6	-	-	-	535.9	-	A1
Me-252	-	538.9	540.5	-	-	-	538.0	-	-	A1
Hopanoid	-	-	-	-	-	-	-	540.0	-	A1
Unknown	-	-	-	-	-	-	541.1	-	-	
Me-252	-	-	-	-	-	-	-	-	542,7	A1
Unknown	-	-	-	-	-	-	-	-	542.7	
C_2-252	-	545.3	-	-	-	-	-	544.7	-	A1

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
DROPPED HEAD, BEGIN SECTIONS HERE
CENTER OF PAGE
TOP OF IMAGE AREA
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

Table 20 (continued).

Compound	1-01-S	1-22-S	2-22-S	2-23-S	1-25-S	2-25-S	1-26-S	2-26-S	2-27-S	Code
Hopanoid	-	-	-	-	-	-	-	544.7	-	A1
Unknown	-	-	-	-	-	-	546.6	-	-	
Hopanoid	-	-	-	-	546.7	546.7	-	-	-	A1
Hopanoid (Norhopane)	-	548.4	549.4	548.5	-	-	-	548.0	-	A
Hopanoid	-	-	-	-	-	-	550.1	-	-	A1
C_2-252	-	-	-	-	-	-	-	-	550.4	A1
Unknown	-	-	-	-	-	-	-	-	550.4	
C_2-252	-	556.1	556.5	554.9	556.5	-	556.8	555.1	-	A1
Unknown	-	-	-	554.9	-	-	-	555.1	-	
p-Quaterphenyl[5]	560.3	563.5	565.4	564.4	563.0	563.0	564.3	564.1	558.8	C
Mixture	-	568.8	-	568.8	567.4	-	-	-	564.2	
Hopanoid	-	-	-	-	570.7	-	-	569.1	-	A1
C_2-252	-	-	-	-	-	-	-	569.1	-	A1
Unknown	-	-	-	-	-	-	569.9	-	-	
Hopanoid (hopane)	-	571.5	-	-	-	-	573.8	572.3	-	A
Unknown	-	-	-	-	-	-	-	-	571.8	
Indeno(1,2,3-cd)pyrene	-	577.2	576.4	576.5	-	-	576.8	-	-	C
Unknown	-	577.2	-	576.5	-	-	-	-	-	
Unknown	-	-	-	-	580.4	-	-	-	-	
Unknown	-	582.0	581.8	582.9	-	-	582.9	-	582.9	
Unknown	-	585.2	586.2	585.3	-	-	-	-	-	
Dibenz(a,h)anthracene	-	585.2	586.2	585.3	-	-	-	-	587.9	C
Unknown	-	595.1	-	588.8	-	-	594.4	-	592.1	
Benzo(ghi)perylene	600	600	600	600	600	600	600	600	600	C

1) EPA/NIH Mass Spectral Data Base, Heller and Milne (eds.), NSRDS-NBS 63 (1978).
2) Registry of Mass Spectral Data, Stenhagen, Abrahamsson and McLafferty (eds.), John Wiley & Sons (1974).
3) Calculated from data of Lee et al. (1979).
4) In cases where substitution is present, it is not always possible to differentiate between substitution on one or more carbon atoms. Thus, C_2, C_3, etc. is used instead of ethyl-dimethyl-, ethyl-methyl- or trimethyl-. Where substituted compounds of structurally different isomers have overlapping ARI's, it sometimes is equally impossible to make a decision to which of the isomers the substituted compound belongs. In such cases, the compound name of the unsubstituted structure is replaced by the molecular weight. "154" thus could be either biphenyl or acenaphthene; "202" could stand for fluoranthene, acephenanthrylene or pyrene, etc.
5) Internal Standard

hydrocarbons. While ECD chromatograms allow an enhanced detection of such compounds, mass spectrometric confirmation for their presence often could not be established because the response turned out to be caused mainly by overlapping hydrocarbons. These problems are discussed in separate paragraph.

A general assessment of the state of pollution within the Chesapeake Bay can be summarized as follows:

1. The organic pollution in sediment of the upper Bay consists mainly of unsubstituted PNAs of pyrogenic origin. These PNAs originate mainly from the combustion of fossil fuels in power generation, home heating, automotive sources and associated highway runoff (Grimmer et. al., 1979; Lee et al., 1977; Lao et al., 1975; Oak Ridge Nat'l Lab., 1979). Baltimore and its harbor appears to be a major source as indicated by the station histograms showing a maximum at the mouth of Baltimore Harbor. Concentrations of some PNAs near the mouth of the Patapsco, similar to those presented here, have been determined by Peterson (1980). Other contributions appear to enter the Bay via the Chesapeake-Delaware Canal and the Severn River. There is litle doubt that substantial contributions are also made by the Susquehanna River, as indicated by the very high concentrations encountered at its mouth in the fall of 1979. However, periodic removal of sediment components containing most of the organic load at times of high water flow rates complicates the collection of meaningful samples, as discussed in a separate paragraph.

Numerous substituted aromatic hydrocarbons in these samples conform with the trends of the pyrogenic unsubstituted PNA fraction and indicate that the same sources may also contribute petroleum hydrocarbons. Very few substituted aromatic hydrocarbons were found in sample 2-27-S (mouth of Susquehanna River, fall 1979), probably due to the preponderance of unsubstituted PNA's.

Midbay stations 19, 18, and 15 appear to be under the influence of the upper Bay, as indicated by the concentration gradient and the compositional similarity.

2. In the lower Bay (south of station 18), most of the organic pollutants appear to concentrate in samples collected within river mouths. Midbay stations 4 and 10 were so clean (only a few compounds present, concentration > 5 ppb) that no further analyses were attempted. The same was true for samples 6 and 7 collected near the southern part of the Eastern Shore and sample 2 collected at Little Creek Inlet. Although the density of the sampling is not sufficient to prove that most of the organic compounds are transported to the Bay by rivers, one is tempted to use this interpretation. Samples 9, 12, 14 and 16 contained enough organic material to warrant HPLC separation, but the level of individual compounds was quite low. This is seen from the bar graphs which indicate about 100 ppb or less for the sums (Figure 17) and < 10 ppb for most individual compounds (Figures 19-27). As in the upper Bay, pyrogenic PNAs dominate in these samples, and an array of alkyl substituted aromatic compounds of likely fossil fuel origin (Table 20) makes up the rest. There appears to be more

variability in the relative contribution of these two aromatic hydrocarbon fractions than in upper Bay samples.

The presence or absence of organic pollutants in sediments should not be judged without some knowledge about the mineralogical sediment characteristics, given in Table 21. Since most pollutants of low solubility are likely to be associated with fine particulate matter (organic detritus, silt and clay), a sample consisting of almost pure sand under equivalent rates of pollutant input can be expected to contain lower concentrations of pollutants than a sample that has more silt and clay. Although we have given preference to silt and clay in the collection of these samples, some, such as samples 1, 2, 4, 6, 7, 9, 11, 12 and 27, from cruise 1 contained more than 80% sand. It is not surprising, therefore, that most of these samples contain very low pollutant levels. Where exceptions are found, as in stations 1, 9, and 27, the state of pollution must be serious. Lynnhaven stands out in this respect. Most river mouth sations in the lower Bay, on the other hand, are characterized by sand contents of less than 20% and for this reason have the potential to contain pollutants at higher levels. The same is true for all sample of the upper Bay, with the exception of the sample from the mouth of the Susquehanna River.

It is difficult to exactly account for sediment character data comparisons. As an approximation, we have assumed that organic pollutants are mainly associated with the silt and clay fraction. The concentration sum for all organic compounds in individual stations was than divided (normalized) by the fraction of silt and clay. Results are presented in Figures 28a and 28b. It would appear from these normalized bar graphs that the silt-clay fraction from the Lynnhaven area contained pollutant levels comparable to those from the mouth of Baltimore Harbor and the Chesapeake-Delaware Canal. The apparent concentration of organic compounds in the silt-clay fraction from station 27 is increased substantially by this normalization, but most results for upper Bay samples were changed very little because their silt-clay contents were initially high. Unfortunately, this normalization could not be applied to samples with a high sand content (2, 4, 6, 7 and 10), as the concentrations of individual compounds were too low to be evaluated.

Table 21: Sediment Analysis

Station I.D.	% Gravel		% Sand		% Silt		% Clay	
	Cruise 1	Cruise 2	Cruise 1	Cruise 2	Cruise 1	Cruise 2	Cruise 1	Cruise 2
01-S	0	0.1	87.0	94.7	6.9	2.2	6.1	3.0
02-S	0.8	4.3	95.0	94.5	2.1	0.6	2.0	0.6
03-S	0.2	3.6	41.4	74.3	33.6	10.6	24.8	11.5
04-S	0.2	0.4	98.7	98.3	0.5	0.2	0.5	1.2
05-S	0	0.3	19.0	14.9	48.4	45.5	32.6	39.2
06-S	0.1	0.1	97.7	96.2	0.8	1.4	1.1	2.3
07-S	0.1	0.1	97.0	89.3	1.1	4.8	1.7	5.7
08-S	0.3	2.3	5.0	13.0	57.4	50.9	37.2	33.8
09-S	0	0.2	89.6	84.2	5.1	9.2	4.6	6.4
10-S	3.2	1.7	79.3	72.0	11.2	18.6	6.2	7.8
11-S	0	trace	86.0	85.1	7.9	6.4	6.0	8.4
12-S	0	0.1	88.5	95.8	4.8	1.2	6.7	2.9
13-S	0	0	5.3	2.4	41.0	37.4	53.7	60.3
14-S	0	1.1	26.3	34.0	38.6	31.0	35.1	33.9
15-S	0	0	0.5	0.5	35.2	33.5	64.3	66.0
16-S	0	0	19.0	13.5	58.9	58.2	22.1	28.3
17-S	0	0.2	1.8	1.6	50.5	44.8	47.7	53.4
18-S	0	0	3.3	2.5	47.4	41.9	49.2	55.6
19-S	12.4	12.6	63.5	63.4	7.4	7.1	16.7	16.8
20-S	0	0	16.4	35.6	42.2	32.8	41.4	31.6
21-S	0.1	0.2	5.1	5.2	31.1	27.6	63.8	67.0
22-S	0	0.1	0.3	trace	33.6	27.9	66.1	72.0
23-S	0	--*	1.0	0.8*	34.3	31.3*	64.7	67.9*
24-S	0	0.1	1.1	2.4	36.7	39.8	62.2	57.7
25-S	0.2	0.1	20.0	14.0	48.1	51.3	31.7	34.5
26-S	0	0.2	10.5	15.9	54.9	52.6	36.7	31.4
27-S	1.5	1.2	96.1	80.2	1.2	10.0	1.2	8.6

*This sample contained a large shell fragment listed as gravel: values are recalculated for zero gravel content.

TOTALS NORMALIZED TO SILT/CLAY

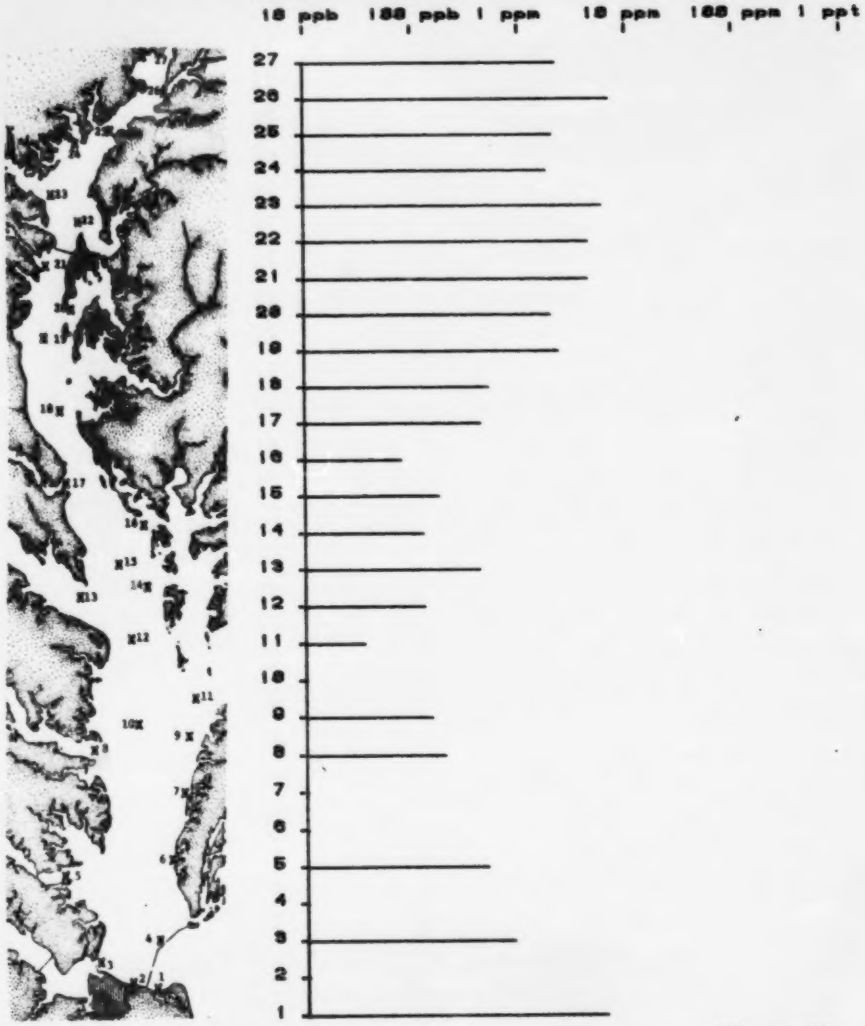


Figure 28a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

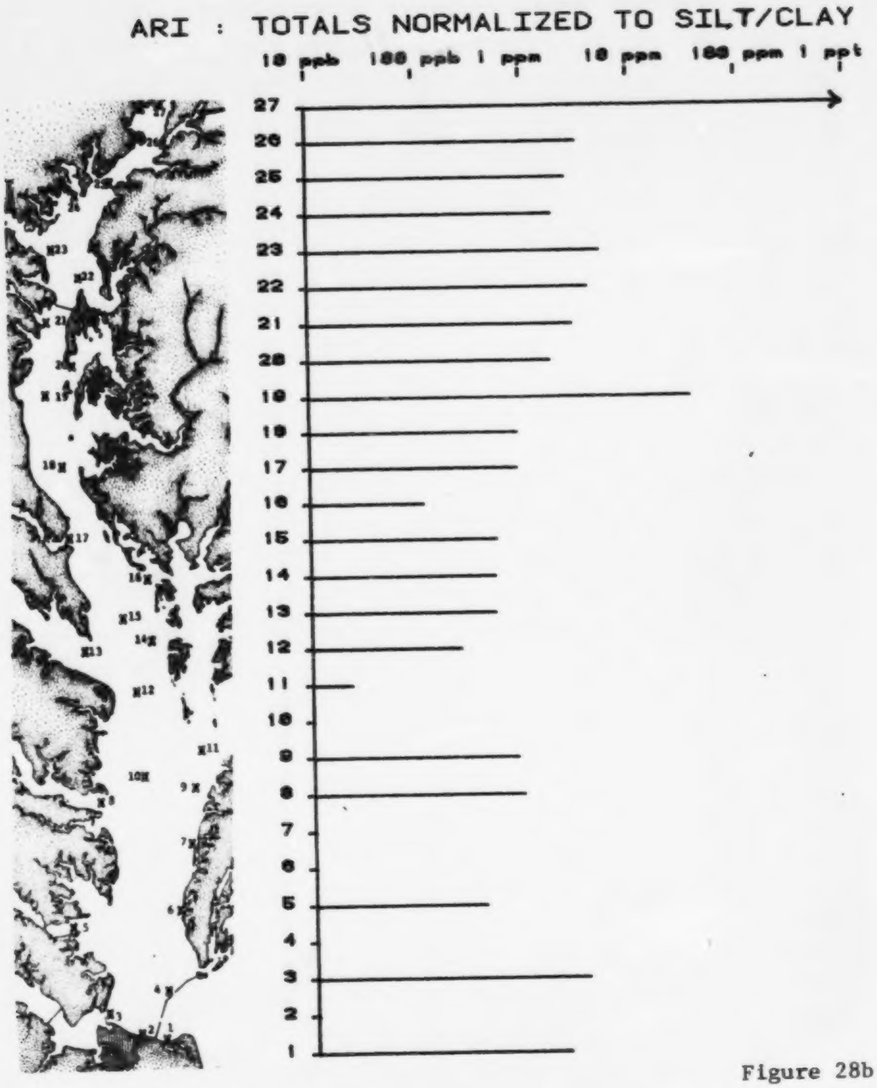


Figure 28b

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

SPECIAL CASES

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

5a. STATION 19

The samples collected at this station were unusual in two aspects. One was a large increase in the overall concentration of organic compounds between the spring and fall samples; the other was a concurrent compositional change. The chromatogram for sample 2-19-S was dominated by a very large peak that was identified (by mass spectrometry and retention) to be p,p'-DDT. o,p'-DDT is also present, but the derivatives p,p'-DDE and o,p'-DDE could not be detected. Also present in abundance were polychlorinated biphenyls (Table 22). Compared to the chlorinated hydrocarbons, the concentrations of PNA's were very small.

2-19-S is the only sample collected in the Bay in which chlorinated hydrocarbons assume such an overpowering presence. From the fact that the DDT derivatives, p,p'-DDE and o,p'-DDE, could not be found, one must conclude that the presence of DDT was the result of a relatively recent dumping operation. The relatively high PCB levels, not found in any of the other samples, point in the same direction.

In view of the drastic changes in the sample compositon between the two cruises, this station and an area surrounding it (Figure 29) was resampled about six and one-half months later (in cooperation with EPA, Annapolis).

Analysis of the G3 fraction by EC (Table 23) indicated p,p'-DDT to be present at levels < 30 ppb, with 20 ppb found in sample MC 1AS (the station closest to station 19). This sample was further separated by HPLC and the presence of p,p'-DDT was confirmed (Table 24).

Sample MC 1AS/G3 displayed a relatively large peak at the retention time of Aldrin (corresponding to 131 ppb relative to an o,p'-DDT standard). This peak was missing in the G32 fraction after HPLC and thus could not have been Aldrin. It was also absent in G31 and G33 of this sample. Sample MC 6AS/G3 gave a peak corresponding to 575 ppb of Aldrin and was selected for analysis by GC-MS. The mass spectra revealed the peak at the retention of Aldrin to be anthraquinone (or anthracenedione), a compound used as a bird repellant. We are unable to explain the absence of this peak in all three HPLC fractions.

The changes in sample composition and concentration occurring at station 19 between the first and the second cruise are likely the result of a narrow local in homogeneity present in the sediments, caused by the dumping of pesticides at high concentration in a container (such as a bag, carton or sheet-metal container) which in time eroded away or was disturbed in the sampling process, thus contaminating the area.

TABLE 22

Compounds identified in sample 2-19-S. Numbers refer to the position of the peak in the chromatogram (in ARI - units).

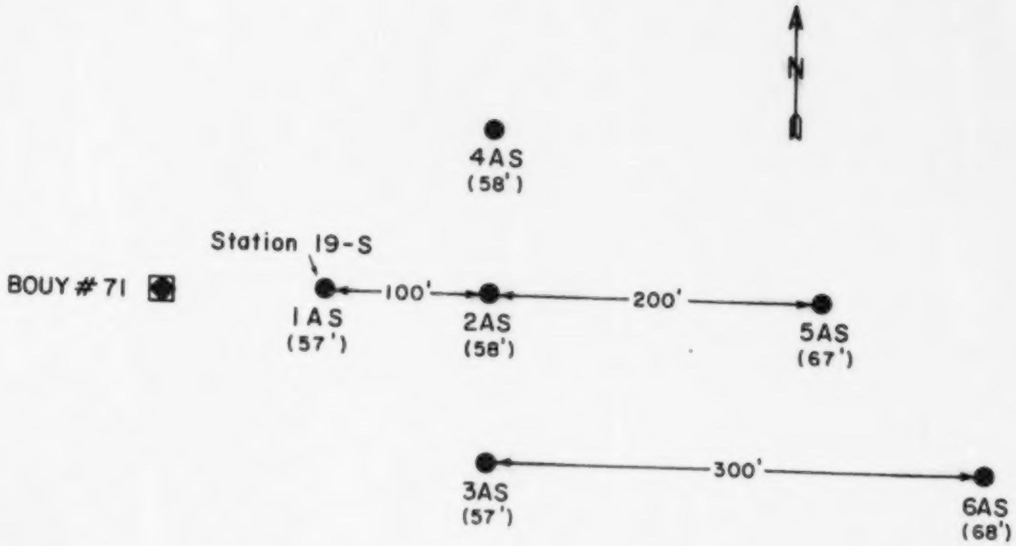
Compound	ARI	
Naphthalene	0	(STD)
2-Me-Naphthalene	53.0	
1-Me-Naphthalene	62.1	
Biphenyl	100.0	(STD)
C_2-Naphthalene	106.2	
C_2-Naphthalene	110.2	
Hexamethylbenzene	118.8	
4-Me-Biphenyl	127.7	
3-Me-Biphenyl	129.7	
Dibenzofuran	134.5	
Fluorene	151.6	
C_2-Biphenyl	162.2	
Cl_2-Biphenyl	162.2	
Me-Dibenzofuran	165.3	
2-Me-Fluorene	181.2	
C_2-Biphenyl	181.2	
1-Me-Fluorene	182.6	
Cl_2-Biphenyl	182.6	
9-Fluorenone	190.4	
C_2-Biphenyl	190.4	
C_2-Dibenzofuran	191.9	
C_3-Biphenyl	191.9	
Cl_3-Biphenyl	191.9	
Dibenzothiophene	193.6	
Phenanthrene	200.0	(STD)
Cl_3-Biphenyl	204.1	
Unknown	207.7	
Cl_3-Biphenyl	215.4	
C_2-Fluorene	215.4	
Me-Dibenzothiophene	223.4	
Cl_3-Biphenyl	227.0	
1,4-Dihydro-1,4-Ethanoanthracene	227.0	
Me-Dibenzothiophene	230.0	
Cl_3-Biphenyl	232.4	
3-Me-Phenanthrene	237.1	
2-Me-Phenanthrene	238.5	
Cl_3-Biphenyl	238.5	
Me-Phenanthrene	244.2	
1-Me-Phenanthrene	245.5	
Cl_4-Biphenyl	245.5	
Cl_4-Biphenyl	254.6	
Cl_4-Biphenyl	256.9	
Phenylnaphthalene	261.2	

Table 22(cont.)
Compounds identified in sample 2-19-S
-2- (continued)

Cl_4-Biphenyl	266.3	
Cl_4-Biphenyl	268.2	
Cl_4-Biphenyl	273.2	
C_2-Phenanthrene	278.2	
Cl_4-Biphenyl	278.2	
C_2-Phenanthrene	280.2	
Cl_4-Biphenyl	280.2	
Fluoranthene	284.8	
Cl_4-Biphenyl	286.9	
Cl_4-Biphenyl	289.8	
Cl_5-Biphenyl	289.8	
Cl_5-Biphenyl	292.7	
Cl_5-Biphenyl	295.5	
Pyrene	300.0	(STD)
Cl_5-Biphenyl	304.4	
Cl_5-Biphenyl	306.6	
Cl_5-Biphenyl	309.4	
Cl_5-Biphenyl	313.0	
Cl_6-Biphenyl	313.0	
Cl_5-Biphenyl	316.2	
Cl_5-Biphenyl	319.6	
Cl_5-Biphenyl	323.1	
p,p'-DDE	327.0	
Cl_6-Biphenyl	327.0	
Cl_5-Biphenyl	330.1	
Cl_6-Biphenyl	337.4	
Cl_6-Biphenyl	340.0	
Cl_6-Biphenyl	345.5	
Cl_6-Biphenyl	351.8	
p,p'-DDD	354.7	
o,p'-DDT	354.7	
Cl_6-Biphenyl	357.3	
Cl_6-Biphenyl	361.7	
Cl_6-Biphenyl	365.6	
Cl_7-Biphenyl	368.6	
p,p'-DDT	379.6	
Cl_6-Biphenyl	379.6	
Cl_7-Biphenyl	383.7	
Unknown (M.W. 226)	385.9	
Cl_7-Biphenyl	385.9	
Cl_7-Biphenyl	388.2	
Cl_7-Biphenyl	391.2	
Cl_6-Biphenyl	393.9	
Cl_7-Biphenyl	397.0	
Chrysene	400.0	(STD)
Cl_7-Biphenyl	401.8	
Cl_7-Biphenyl	404.6	
Cl_7-Biphenyl	407.4	
Cl_8-Biphenyl	410.7	

Table 22(cont.)
Compounds identified in sample 2-19-S
-3- (continued)

Cl_7-Biphenyl	413.6	
Cl_7-Biphenyl	417.6	
Cl_7-Biphenyl	420.9	
Cl_8-Biphenyl	423.4	
Cl_7-Biphenyl	433.6	
Cl_8-Biphenyl	438.5	
Cl_8-Biphenyl	441.1	
Cl_7-Biphenyl	449.5	
Cl_8-Biphenyl	457.3	
Cl_8-Biphenyl	468.4	
Cl_8-Biphenyl	470.9	
Benzo(j,b,k)Fluoranthenes	475.4	
Cl_9-Biphenyl	488.7	
Benzo(e)Pyrene	491.9	
Perylene	500.0	(STD)
Unknown Chlorinated Compound	543.7	
"	547.9	
"	549.6	
p-Quaterphenyl	567.1	
Unknown Chlorinated Compound (M.W. 502)	576.5	
"	580.7	
"	585.7	
Unknown (M.W. 276)	585.7	
Unknown Chlorinated Compound (M.W. 502)	588.8	
"	593.9	
"	596.4	
Benzo(ghi)Perylene	600.0	(STD)


N
4AS
(58')
Station 19-S
BOUY # 71
1AS
(57')
100'
2AS
(58')
200'
5AS
(67')
3AS
(57')
300'
6AS
(68')

"Location of additional sampling sites near station 19-S (June 2, 1980)."

Figure 29

TABLE 23

Data on additional samples collected near station 19-S (derived from wallcoated glass capillary columns and E.C. detector; concentrations based on external standards).

G3 fraction (all concentrations in ppb).

Compound Identification (by retention)	Station Identification: MC					
	1AS	2AS	3AS	4AS	5AS	6AS
Aldrin	113	35	58	90	71	575
o,p'-DDE	1	<1	2	1	1	1
Dieldrin	1	<1	<1	<1	<1	<1
p,p'-DDE	7	2	<1	<1	1	2
o,p'-DDD	7	2	4	3	3	3
m,p'-DDD	3	2	2	2	1	1
o,p'-DDT p,p'-DDD	11	1	1	1	1	3
p,p'-DDT	20	3	30	6	2	13

TABLE 24

G31, G32 and G33 HPLC fraction of sample MC 1AS

Compound Identification (by retention)	G31	G32	G33
Aldrin	-	-	-
o,p'-DDE	-	1	1
Diedrin	1	1	1
p,p'-DDE	-	8	-
o,p'-DDD	4	7	3
m,p'-DDD	2	3	1
o,p'-DDT p,p'-DDD	3	9	-
p,p'-DDT	-	15	4

5b. STATION 27

The spring sample collected at the mouth of the Susquehanna River did not show anything unusual. Main components were unsubstituted PNA's of pyrogenic origin, with concentrations of a few ppb for individual compounds. The sample collected during fall, however, was different. Although pyrogenic PNAs again were standing out as major sample components, their concentrations were higher than those in the first sample, in some cases by factors of about 10,000. They exceed the concentrations reported by Laflamme and Hites (1978) reported for the Charles River.

In view of these unusual results, three more aliquots of this sediment were extracted and all analyses confirmed the presence of PNA's at such extreme levels. A GC-MS anlaysis of the polar fraction (G33) in addition revealed the presence of carbazole (at ppm levels) and benzocarbazoles in this sample.

A summary of the G32 analyses is found in Table 25. This table in addition contains the results for sediment samples that were collected about six and one-half months later with the assistance of Dr. Owen Bricker near station 27 (samples MC 1BS to MC 6BS), and two soil samples (MC DCS and MC DES) collected near a dump draining into the Susquehanna close to its mouth. The location of these additional sampling sites is shown in Figure 30.

Although the PNA concentrations in these later collections clearly are much lower than in sample 2-27-S, they are enhanced relative to the first sample. The highest concentrations are encountered in the deepest part of the river mouth north of station 27 (1BS, 4BS and 6BS), while samples closer to shore (3BS and 5BS) or south of station 27 (2BS) contain the same PNA's at considerably lower concentration. Both soil samples from the dump area also contain pyrogenic PNA's similar to those encountered in the sediment samples, and at concentrations that are about comparable to those in the river channel, but there are compositional differences present.

There is little question that the changes in PNA concentrations were related to the nature of the sediments that were collected. Some characteristics were so obvious that they could be observed after freeze drying. The surface sediment collected, for example, during cruise 1 at station 27 consisted of almost pure sand sized particles. But the same location sampled in cruise 2 had a muddy appearance and contained about 20% of silt/clay. All sediments collected six and one-half months later had an approximately 2-3 cm layer of fine-grained material deposited on top of sand (only this layer of muddy appearance, however, was collected for analysis, so that the actually extracted samples for 2-27-S and MC 1-6 BS with respect to their sedimentological classification were not too different). A reason for these changes in sediment character may be found in observed flow rate changes in the Susquehanna River. Figure 31 (taken from M. Nichols report) indicates unusually large flow rates just before sample 1-27-S was collected. Excessive scouring related to these flow rates may have removed most of the silt/clay originially deposited on top of the sand. This could explain why this sample consists almost

Table 25. Quantitation of Aromatic Compounds Extracted from Sediments near Susquehanna River Mouth

Notes:
1. Aromatic compounds eluted between biphenyl and benzo(ghi)perylene were quantified
2. Flame ionization detector
3. "Pyrogenic" PNA's were marked by *

ARI	Possible Identification	Concentration (ppb in binaphthyl equivalent) 1-27-S	2-27-S	MC 1BS	MC 2BS	MC 3BS	MC 4BS	MC 5BS	MC 6BS	HG DCS	HG DES
100	*Biphenyl	1.4	-	-	-	-	-	-	-	8.4	23
106.4	2,6-Dimethyl Naphthalene	-	-	8.4	-	2.8	4.8	2.9	8.6	39	12
110.6	1,3-Dimethyl Naphthalene	-	-	-	-	-	-	-	-	14	5.8
115.6	1,4-/1,5-Dimethyl Naphthalene	-	-	-	-	-	-	-	-	7.9	-
128.9	Acenaphthene	-	-	4.3	-	-	-	-	3.9	17	7.4
152.2	Fluorene	1	-	13	-	-	11	-	11	7.7	6.3
183.1	1-Methyl Fluorene	-	-	6.9	-	-	-	-	5.6	14	-
193.5	Dibenzothiophene	-	5900	8.3	-	-	-	-	6.9	11	11
200	*Phenanthrene	4.8	95000	100	15	2.8	69	18	88	85	150
203.1	*Anthracene	-	5300	13	-	-	12	-	16	8.7	9.2
231	Methyl Dibenzothiophene	-	-	7.6	-	-	-	5	5.2	15	3.7
236	Methyl Phenanthrene	-	-	19	-	2.9	16	3.7	17	32	11
238	Methyl Phenanthrene	-	-	27	4.8	3.7	21	4.9	23	53	19
244	Cyclopenta(def)phenanthrene	-	9900	10	-	-	9.2	-	8.6	22	7.0
245	Methyl Phenanthrene	-	8600	12	-	-	10	-	8.8	14	8.4

Table 25 (continued).

ARI	Possible Identification	Concentration (ppb in binaphthyl equivalent)									
		1-27-S	2-27-S	MC 1BS	MC 2BS	MC 3BS	MC 4BS	MC 5BS	MC 6BS	HG DCS	HG DES
261	C_2-Dibenzothiophene	2.1	5100	8.8	-	-	12	2.9	8.9	23	97
285.5	*Fluoranthene	3.5	180000	150	41	17	120	28	160	110	110
300	*Pyrene	3.4	130000	150	41	17	120	28	140	84	97
304	Methyl Phenylnaphthalene	-	21000	17	7.3	-	15	3.4	24	12	17
314.5	C_3-Phenanthrene	-	-	12	-	-	10	-	8.1	19	24
321.5	"	-	-	20	-	-	12	3.1	14	18	27
331	Benzo(a)fluorene	1.2	5000	54	8.9	3.7	19	5.0	48	61	7.1
336	Benzo(b)fluorene	-	23000	40	-	-	-	7.2	6.7	36	6.3
345.8	Methylpyrene	-	5900	14	-	-	11	-	11	13	5.4
366.7	C_2-Acephenanthrene	-	8200	26	4.5	-	23	3.7	22	43	9.8
397.1	*Benz(a)anthracene	-	47000	60	22	7.9	54	11	61	47	48
400	*Chrysene + Triphenylene	4.4	69000	110	35	15	97	18	100	100	76
404	Methyl Benzo(b)naphthothiophene	1.1	9100	12	10	-	15	4.0	20	-	-
408	" "	2.8	-	7.3	12	-	-	4.1	9.1	7.8	5.5
412	" "	1.7	5500	6.6	-	-	-	-	6.3	7.6	4.0
475	*Benzo(b,j,k)fluoranthenes	-	22000	-	-	-	-	-	-	-	110
491.3	*Benzo(e)pyrene	-	49000	68	22	9.7	56	10	54	55	13
494.3	*Benzo(a)pyrene	3.1	73000	77	18	12	70	12	59	29	44
500	Perylene	3.0	24000	56	23	9.2	33	14	74	26	19

Table 25 (continued).

ARI	Possible Identification	Concentration (ppb in binaphthyl quivalent) 1-27-S	2-27-S	MC 1BS	MC 2BS	MC 3BS	MC 4BS	MC 5BS	MC 6BS	HG DCS	HG DES
578	Indeno(1,2,3-cd)pyrene	-	53000	63	19	11	61	9.5	51	37	30
588	Dibenz(a,h)anthracene	-	11000	15	6.2	-	13	-	4.4	8.8	6.9
600	*Benzo(ghi)perylene	-	43000	68	26	12	59	9.7	47	35	29
Sum of pyrogenic PNA/sum of all compounds		0.38	0.64	0.33	0.56	0.57	0.62	0.29	0.45	0.29	0.30
Sum of identified Aromatics/sum of all compounds		0.61	0.81	0.52	0.80	0.77	0.86	0.44	0.70	0.58	0.45

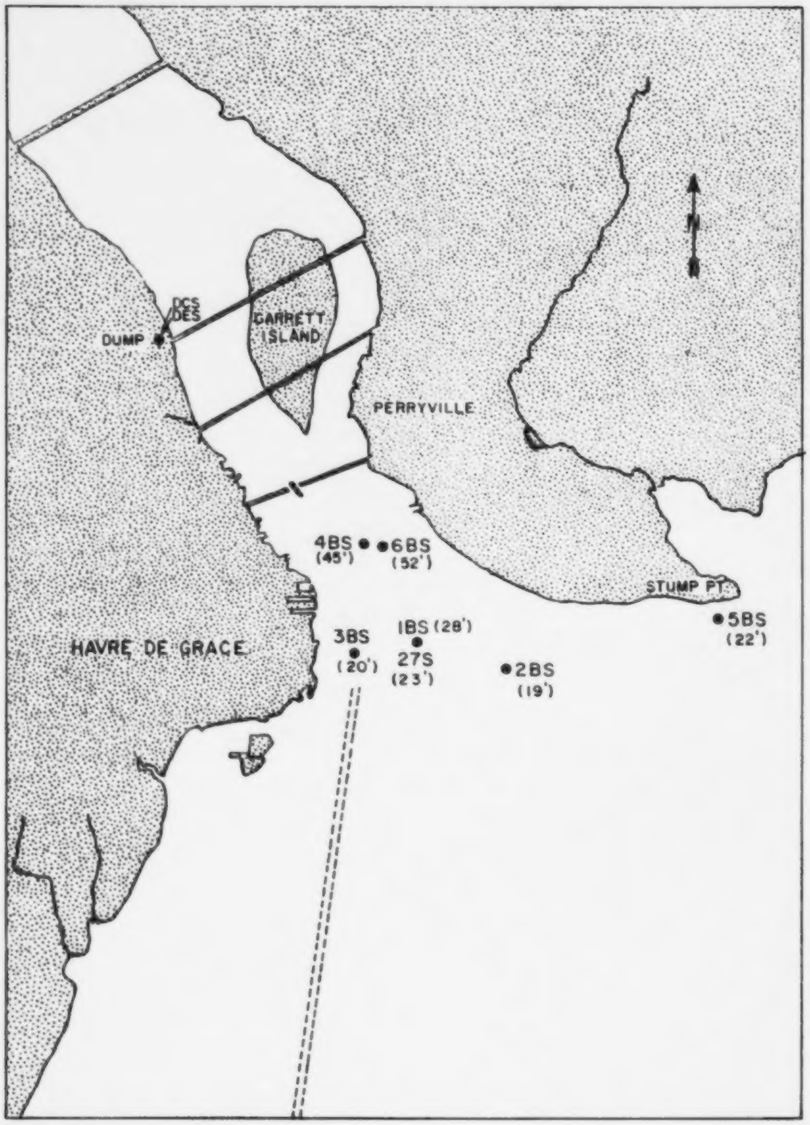

N
DCS
DES
DUMP
GARRETT ISLAND
PERRYVILLE
4BS (45')
6BS (52')
STUMP PT.
5BS (22')
3BS (20')
1BS (28')
27S (23')
2BS (19')
HAVRE DE GRACE

Figure 30. Location of additional sampling sites near station 27-S (June 2, 1980)

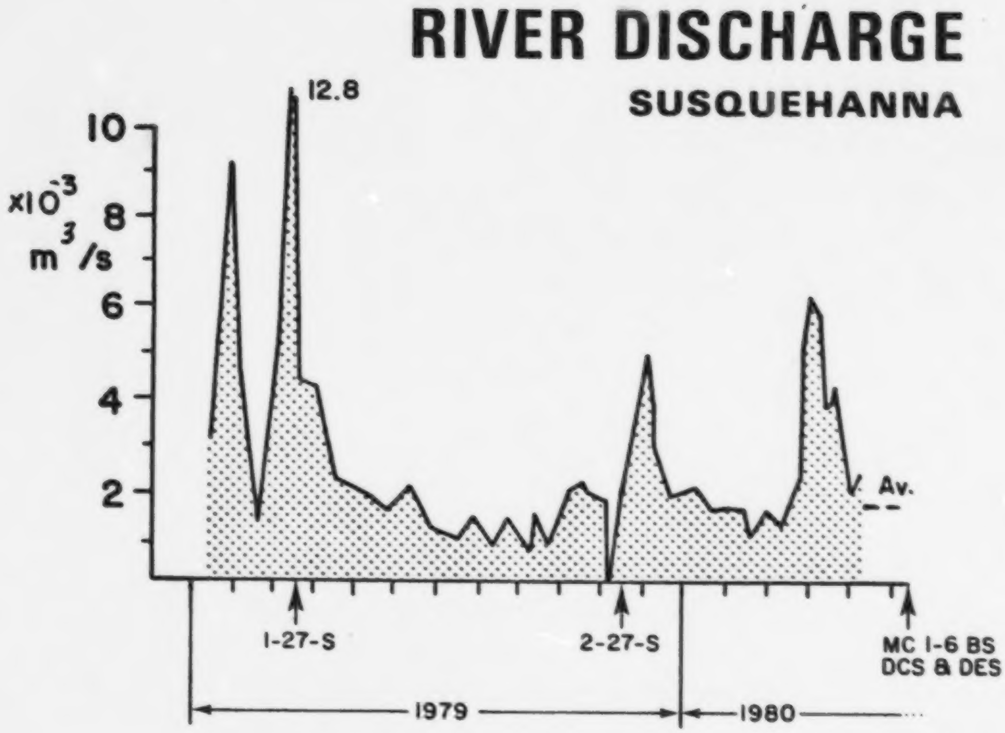

RIVER DISCHARGE
SUSQUEHANNA
12.8
10
8
6
4
2
x10^-3 m^3/s
Av.
1-27-S
2-27-S
MC 1-6 BS
DCS & DES
1979
1980

Figure 31

exclusively of sand. Similarly, a much lower than average flow rate occurred just before the collection of sample 2-27-S, a condition that could be favorable for the settling and continuous depositon of originally suspended silt/clay particles, thus explaining the enhanced silt/clay sample collected at this location during the second cruise. Flow rates increased again above average after this sample was collected until about the middle of December 1979, and again between about the middle of March and end of April 1980. These two flow maxima, however, were only about 1/3 to 1/2 of the large maximum at the beginning of March 1979, so that scouring may have been less extensive, affecting only the finest particles (which may be the main carriers of PNA fractions). The near uniformity of the samples collected in June 1980 over an extended area around station 27 would suggest that spatial differences may not be very important in this case and that temporal variations in the sediment character are much more important.

Although many of these details can only be guessed at, we believe they are a good example of the limitations inherent in the analysis of organic compounds in single sample collections. These observations and data clearly show that Bay sediments are not static but change continually, responding not only to catastrophic events like tropical storm Agnes, but to relatively small seasonal or in some areas maybe even tidal changes. Areas that are sinks for organic pollutants at some times of the year may become sources at other times. Particles under such circumstances may become an important vehicle for pollutant transport.

6. OYSTER SAMPLES

It was evident from the chromatograms that oyster tissue extracts were much less complex than those from sediments, and that the concentration of individual compounds was substantially lower than in sediments. These original observations were confirmed after processed data sets were inspected. To discuss the oyster extracts in more detail, we again present a data summary in the form of bar graphs (Figures 32 to 35). The bar graphs in which the concentrations representing the sum of all peaks are plotted (Figures 32a and b) immediately convey the fact that there are no visible trends similar to those in the corresponding sediment histograms.

The mass spectrometric analyses in Table 26 show that the oyster extracts contain many compounds whose structure we could not identify. In addition, methylesters of C_{14} and C_{16} fatty acids were present in most samples, as were some ketones. We can only hypothesize that many of these compounds have a biogenic origin, and since they are often present in higher concentration than identified pollutants, the sum-histograms to some extent may not represent the pollutant content in oysters. It is perplexing to note the lack of correlation between oyster samples and sediments. Dibenzothiophene is only found in the bar graphs for samples south of Calvert Cliff (Station 18, Figure 33). This compound in sediments is definitively more prominent in the upper Bay (Figure 19). Of the PNA's, only two (fluoranthene and pyrene) were found to be present in oysters from several locations. Benzo(e)pyrene was identified in stations 2-03-B and 2-22-B (Table 26). No benzo(a)pyrene could be detected in the same samples.

Table 26 also indicates the presence of several chlorinated compounds which were not encountered in sediments. While these may be metabolities or the result of bioconcentration, it is also possible that they are artifacts of the analysis which could not be seen in the sediment extracts because they were masked by high hydrocarbon levels.

The main problem encountered in the analysis of oyster tissues was the presence of biogenic compounds and their derivatives, often commanding a major presence in the chromatograms. Their retention relative to unsubstituted PNA's (as routinely used for the G32 fraction) turns out to be ill-defined. Retention indices of these compounds appear to be precise for a particular column as one notes in Table 26, but may vary (up to six retention units) if different columns are used. Since specific searches are based on ARI's, interpolation of chromatograms bracketed by GC-MS analyses in this case is not reliable and may lead to false conclusions. A simple remedy would be to analyze such fractions on one GC-column only.

FIGURES 32-35: Station histograms for samples of oyster tissue collected during spring (a) and fall (b). The station locations and station numbers are indicated in the map. The vertical axis of the histograms contains the station numbers, the horizontal axis the concentrations on a logarithmic scale. Concentrations <10 ppb were omitted.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER

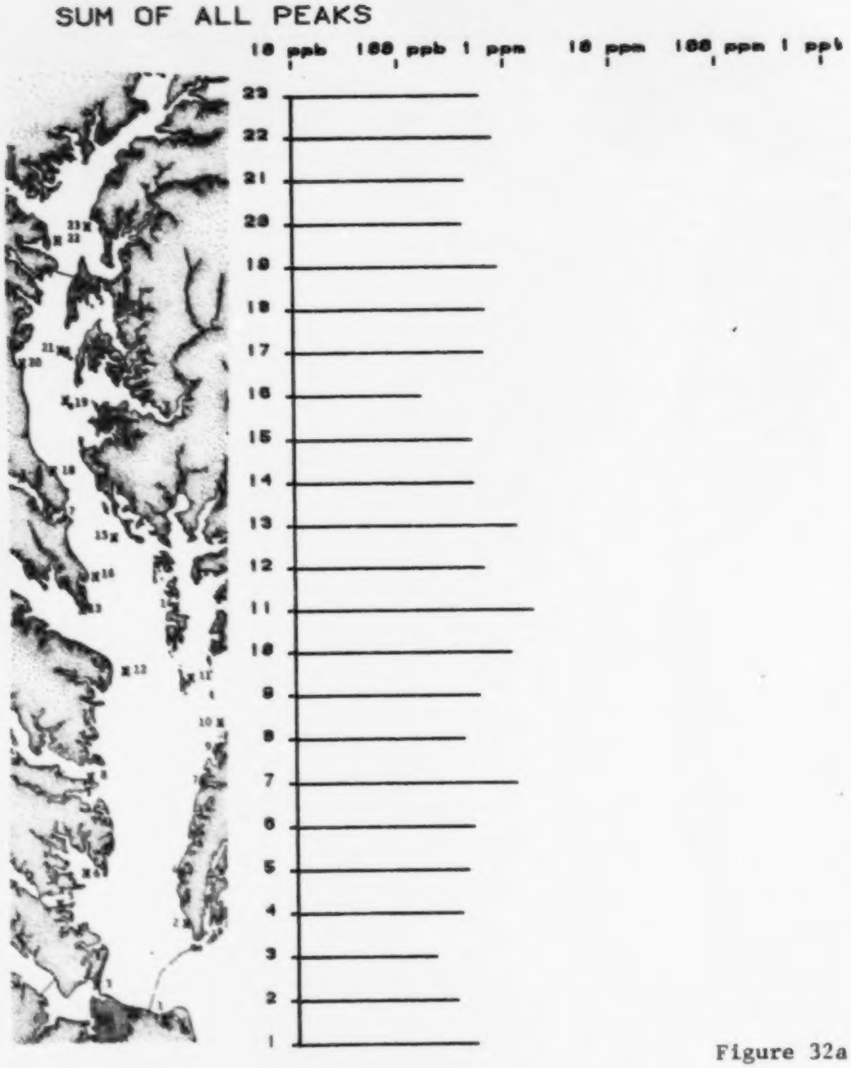
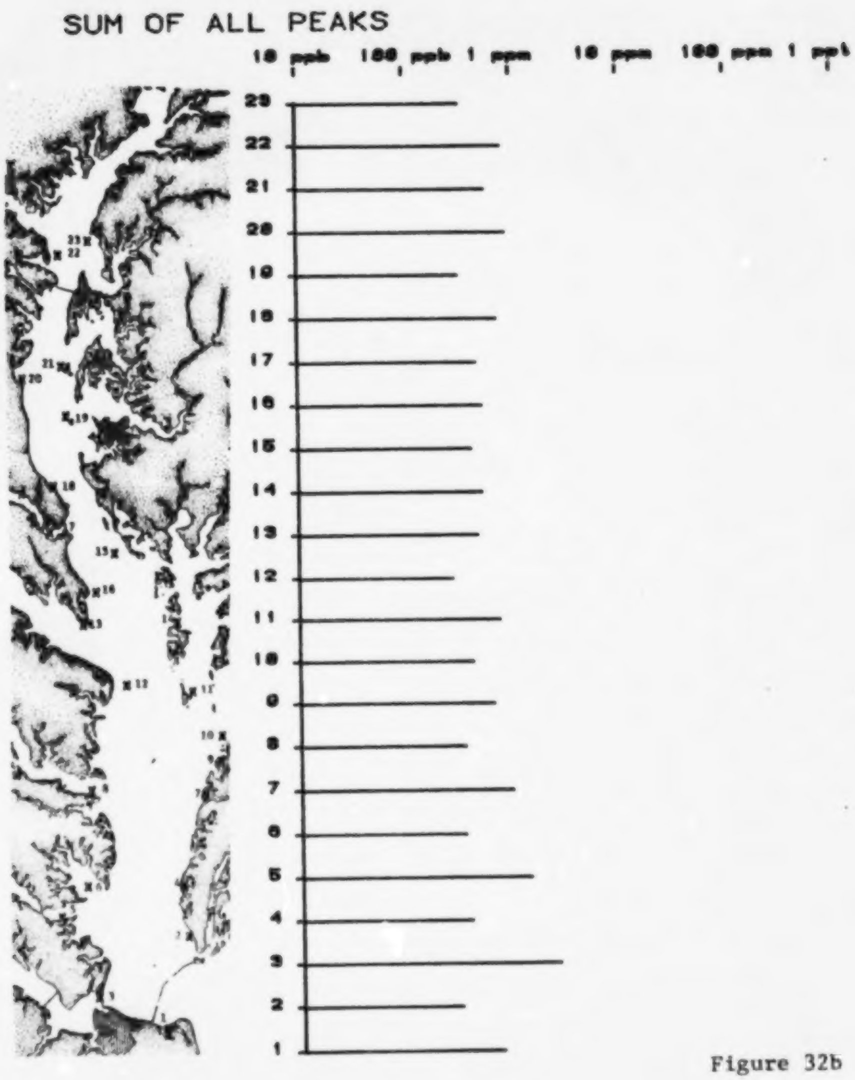

SUM OF ALL PEAKS
10 ppb
100 ppb
1 ppm
10 ppm
100 ppm
1 ppt
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 32a



SUM OF ALL PEAKS

Figure 32b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER

ARI : 192-196 Dibenzothiophene

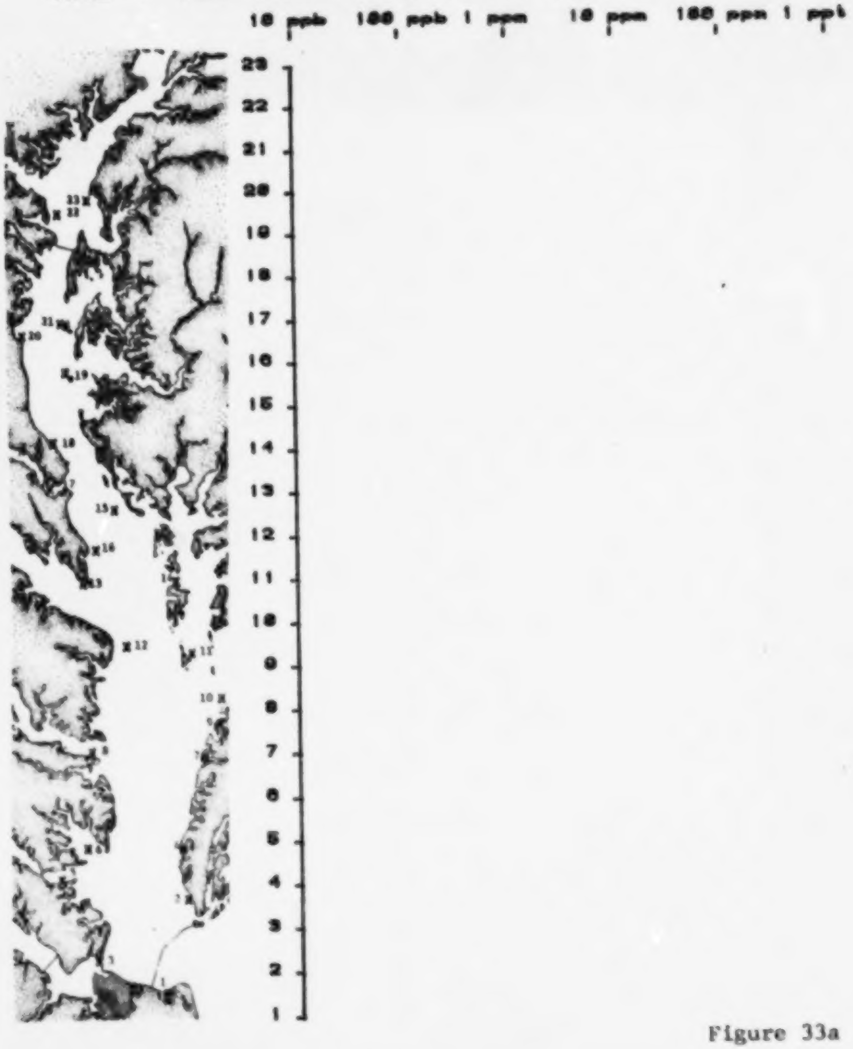


Figure 33a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-79)

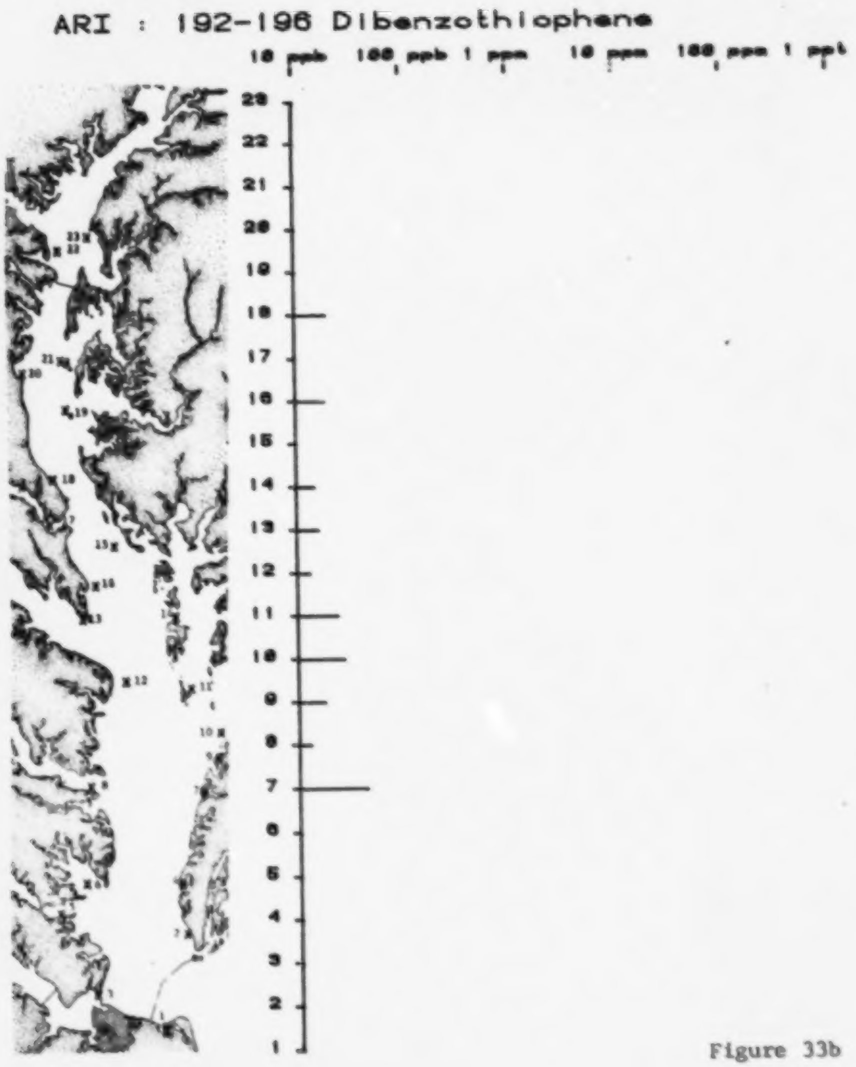


Figure 33b

MAIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER

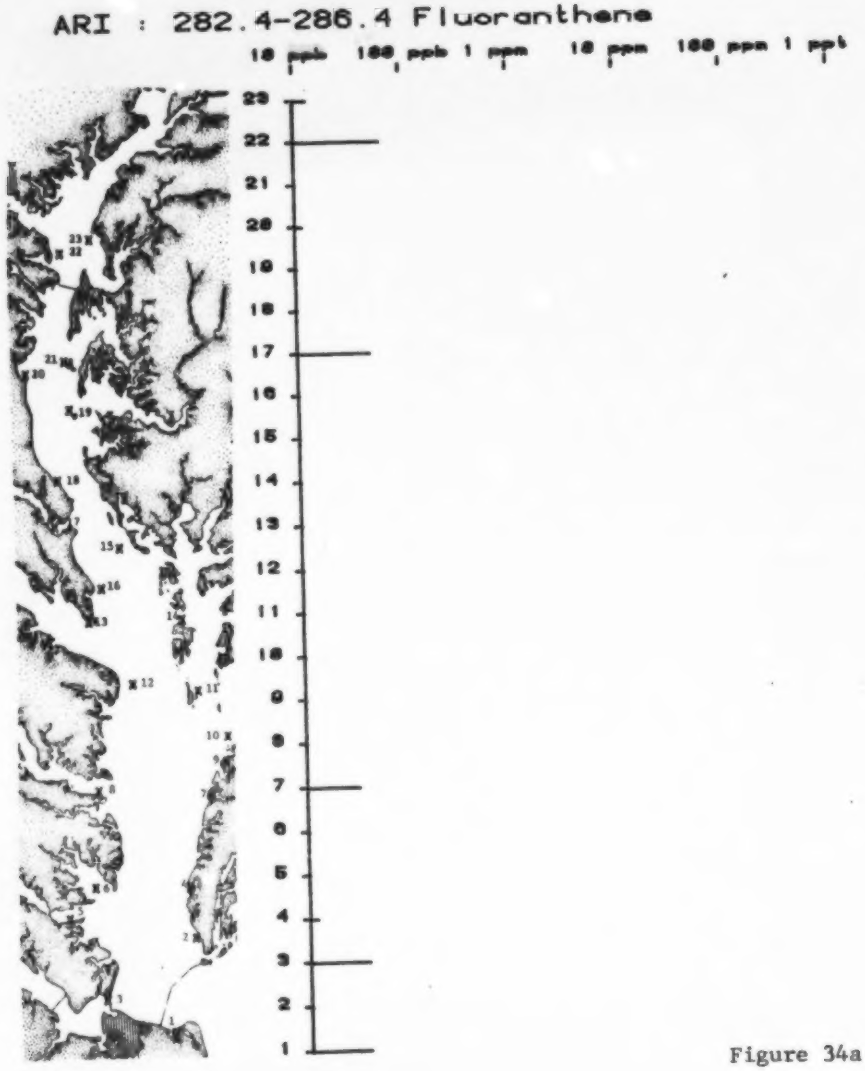


Figure 34a

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

ARI : 282.4-286.4 Fluoranthene

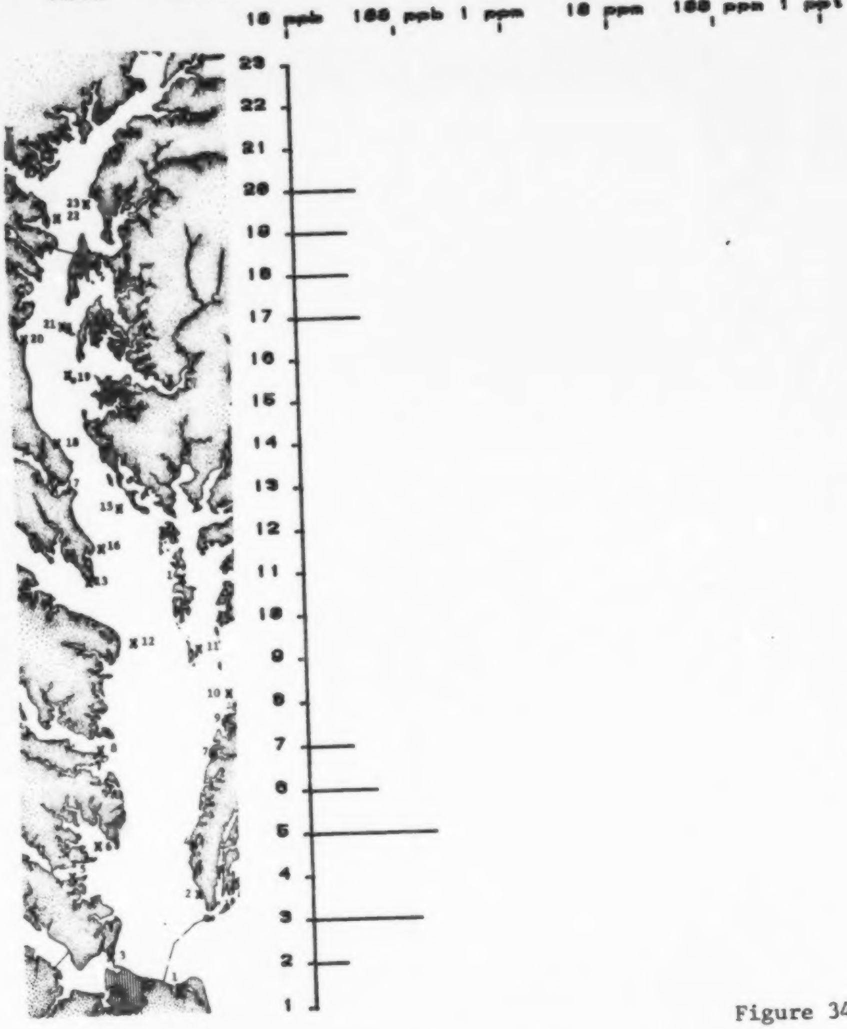


Figure 34b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

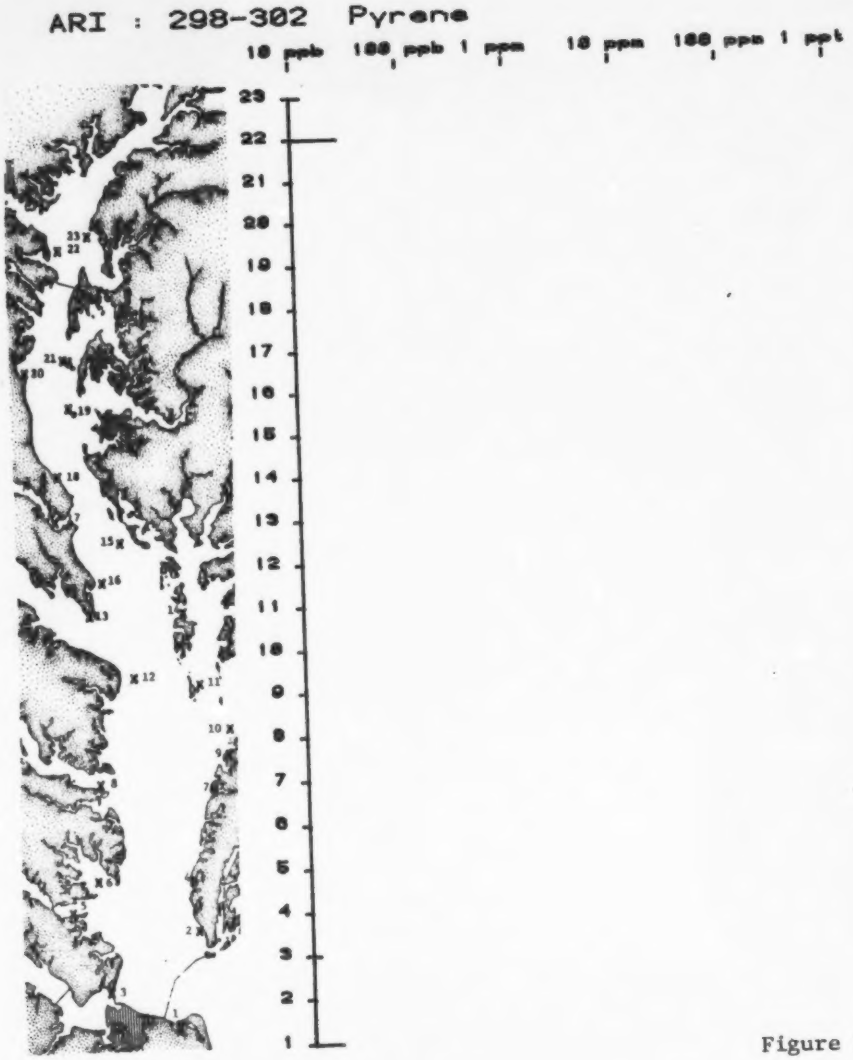


Figure 35a

BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

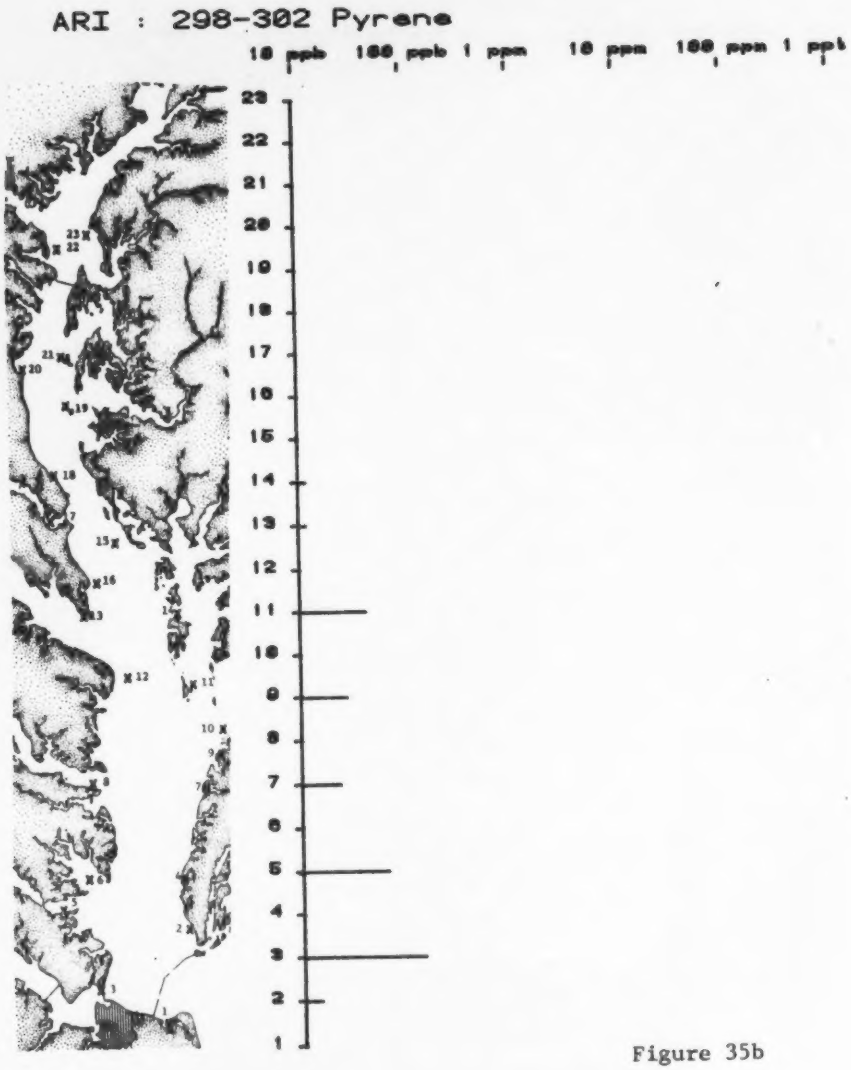


Figure 35b

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

Table 26. Compounds identified by mass spectrometry - oyster samples. Numbers relate to position of peak in the chromatograms (in ARI units). Code: A - identified by comparison with reference spectrum[1,2];A1 - by interpretation of mass spectrum; B - by mass spectrum and published ARI[3];C - by mass spectrum and ARI established by standard in our laboratory; D - by mass spectrum and ARI extrapolated from crude oil sample.

Compound	Station							Code
	1-02-B	2-03-B	1-07-B	2-07-B	1-10-B	2-20-B	2-22-B	
Unknown A	+	3.5	-	+	+	3.3	3.2	
Unknown A1	-	15.2	-	-	-	15.9	15.7	
Unknown B	+	-	-	-	+	-	-	
Cis-4-Phenyl-3-buten-2-one	-	36.9	-	-	-	37.6	37.9	A
Unknown C	+	42.0	-	+	+	42.2	41.5	
Unknown D	+	72.4	75.0	+	+	72.9	72.3	
Unknown E1	+	-	-	-	-	-	-	
Unknown E2	-	-	84.7	+	+	-	-	
trans-4-Phenyl-3-buten-2-one	-	89.8	-	+	-	89.2	90.5	C
Unknown F1	103.9	104.2	-	104.0	103.9	103.7	103.8	
Unknown F2	103.9	104.2	-	104.0	103.9	103.7	103.8	
Unknown F3	-	-	104.4	-	-	-	-	
Alkane	106.3	-	-	-	-	-	-	A
Unknown G	-	-	-	-	-	-	109.8	
3-Methoxy-2-naphthalenol	-	127.9	-	-	-	-	-	A
Alkane	133.1	-	-	-	-	-	-	A
C_3-Naphthalene	-	133.7	-	-	-	-	-	D
Unknown H	139.6	139.6	141.0	139.6	139.5	139.6	139.3	
Unknown I	-	-	-	-	144.6	-	-	
Unknown I1	-	145.0	-	-	-	-	-	
C_3-Naphthalene	-	147.6	-	-	-	-	-	B,C
Isomer of H (Unknown H1)	-	-	158.7	-	-	-	-	
Unknown J	158.3	-	160.1	-	158.0	-	-	
Alkane	-	-	-	-	-	158.9	158.2	A
Unknown K	-	158.5	-	-	-	-	-	
N-Phenylbenzylamine/Biphenylamine	-	163.6	-	-	-	-	-	A
Alkane	-	-	-	163.6	-	-	-	A
C_4-Naphthalene	-	174.8	-	-	-	-	-	D
C_5-Naphthalene	-	177.7	-	-	-	-	-	A1
C_4-Naphthalene	-	179.7	-	-	-	-	-	D
Pyrazol-3-ol,5-phenyl acetate/3-pyrazolin-5-one,2-acetyl-3-phenyl	-	181.7	-	-	-	-	-	A
Methyl Fluorene	-	182.6	-	-	-	-	-	B,C
Alkane	-	-	-	-	183.0	-	-	A
3,4-Dihydro-3,3,6,8-tetramethyl-1-(2H)-naphthalenone	-	187.5	-	-	-	-	-	A
Methyl Tetradecanoate	-	-	192.6	190.0	189.2	190.0	-	A

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

Table 26 (continued).

Compound	Station							Code
	1-02-B	2-03-B	1-07-B	2-07-B	1-10-B	2-20-B	2-22-B	
C_4-Naphthalene	-	190.1	-	-	-	-	-	A1
C_3-Biphenyl/C_3-Acenaphthene/C_2-Dibenzofuran	-	190.1	-	-	-	-	-	A1
C_3-Biphenyl/C_3-Acenaphthene/C_2-Dibenzofuran	-	191.7	-	-	-	-	-	A1
Dibenzothiophene	193.7	193.4	-	193.5	193.7	-	-	B,C
Unknown L	204.8	-	-	-	204.6	205.6	205.0	
C_2-Fluorene	-	213.0	-	-	-	-	-	D
C_2-Fluorene	-	217.1	-	-	-	-	-	D
C_5-Naphthalene	-	217.1	-	-	-	-	-	A1
C_2-Fluorene	-	221.0	-	-	-	-	-	D
C_3-Biphenyl/C_3-Acenaphthene/C_2-Dibenzofuran	-	221.0	-	-	-	-	-	A1
C_4-Biphenyl/C_4-Acenaphthene/C_3-Dibenzofuran	-	221.0	-	-	-	-	-	A1
Methyl pentadecanoate	-	-	222.6	-	-	-	-	A
Me-Dibenzothiophene	-	223.7	-	-	-	-	-	D
C_4-Biphenyl/C_4-Acenaphthene/C_3-Dibenzofuran	-	226.0	-	-	-	-	-	A1
C_4-Biphenyl/C_4-Acenaphthene/C_3-Dibenzofuran	-	227.9	-	-	-	-	-	A1
Me-Dibenzothiophene	-	230.5	-	-	-	-	-	D
C_5-Naphthalene	-	234.1	-	-	-	-	-	A1
3-Me-Phenanthrene	-	237.2	-	237.0	237.9	-	-	B
2-Me-Phenanthrene	238.4	238.5	-	-	-	-	238.4	B
Me-Phenanthrene	-	245.4	-	-	-	-	-	B
Methyl ester of C16:1 acid	-	-	247.0	-	-	-	-	A
Methyl Hexadecanoate	-	-	254.0	249.5	248.7	250.0	249.4	A
C_3-Fluorene	-	249.8	-	-	-	-	-	D
C_5-Naphthalene	-	253.2	-	-	-	-	-	A1
C_2-Dibenzothiophene	-	255.5	-	-	-	-	-	A1
C_2-Dibenzothiophene	-	260.3	-	-	-	-	-	A1
2-Phenylnaphthalene	-	-	-	-	260.6	-	-	B,C
C_2-Dibenzothiophene	-	261.9	-	-	-	-	-	D
C_3-Fluorene	-	264.9	-	-	-	-	-	A1
C_2-Dibenzothiophene	-	268.7	-	-	-	-	-	D
C_2-Phenanthrene	-	274.2	-	-	-	-	-	B,D
Unknown M	-	277.3	-	275.7	-	-	-	
C_2-Phenanthrene	-	279.1	-	-	278.4	-	-	D
C_2-Phenanthrene	-	280.9	-	-	-	281.8	-	D
C_3-Dibenzothiophene	-	282.9	-	-	-	-	-	D
Fluoranthene	285.2	285.5	285.7	285.2	285.2	-	285.3	B,C
C_3-Dibenzothiophene	-	289.6	-	-	-	-	-	D
C_3-Dibenzothiophene	-	295.3	-	-	-	-	-	A1

Table 26 (continued).

Compound	Station							Code
	1-02-B	2-03-B	1-07-B	2-07-B	1-10-B	2-20-B	2-22-B	
C_3-Dibenzothiophene	-	303.4	-	-	-	-	-	D
Me-Phenylnaphthalene	-	303.4	-	-	-	-	-	Ai
Cl_5-Biphenyl (2,2',4,5,5'-Pentachloro-1,1'-biphenyl) (M.W. 324)	-	-	-	-	-	305.2	-	A
Chlorinated compound	-	-	-	-	-	308.0	-	Ai
C_3-Dibenzothiophene	-	308.1	-	-	-	-	-	Ai
C_4-Dibenzothiophene	-	308.1	-	-	-	-	-	Ai
C_3-Dibenzothiophene	-	312.5	-	-	-	-	-	Ai
C_4-Dibenzothiophene	-	312.5	-	-	-	-	-	Ai
C_3-Phenanthrene	-	315.0	-	-	-	-	-	D
C_3-Phenanthrene	-	318.1	-	-	-	-	-	D
C_3-Phenanthrene	-	319.8	-	-	-	-	-	D
C_4-Dibenzothiophene	-	319.8	-	-	-	-	-	Ai
C_3-Phenanthrene	-	323.6	-	-	-	-	-	Ai
Unknown N	-	323.6	-	-	-	-	-	
p,p'-DDE	-	326.0	-	323.6	-	324.1	-	C
C_4-Dibenzothiophene	-	326.0	-	-	-	-	-	Ai
Chlorinated compound (Pentachlorobiphenyl) (M.W. 324)	-	329.0	-	-	-	-	-	Ai
C_3-Phenanthrene	-	329.0	-	-	-	-	-	D
9,10-Diethylphenanthrene	-	333.8	-	332.7	332.4	-	-	B
Benzo(b)fluorene/Me-202	-	336.4	-	-	-	-	-	B,C
Chlorinated compound	-	343.3	-	-	-	-	342.6	Ai
Me-202	-	343.3	-	-	-	-	-	Ai
Unknown O	-	-	-	-	-	-	344.3	
Me-202	-	346.2	-	-	-	-	-	Ai
Unknown P	-	-	-	-	-	-	349.6	
Chlorinated compound (M.W. 405)	-	-	-	-	-	350.0	-	Ai
C_4-Phenanthrene	-	358.9	-	-	-	-	-	D
Chlorinated compound (M.W. 358)	-	358.9	-	-	-	-	-	Ai
Unknown Q	-	-	-	-	-	-	364.3	
Chlorinated compound (M.W. 358)	-	375.9	-	-	-	-	-	Ai
Benzonaphthothiophene	377.9	377.4	-	378.1	377.7	-	-	B
C_3-Dibenzothiophene	-	380.4	-	-	-	-	-	Ai
C_2-202	-	385.4	-	-	-	-	-	Ai
Chlorinated compound	-	385.4	-	-	-	-	-	Ai
Unknown R1	386.1	-	-	386.1	-	-	-	A
Unknown R2	-	-	-	-	385.3	-	-	
Unknown R3	-	-	-	-	-	-	386.4	

Table 26 (continued).

Compound	Station							Code
	1-02-B	2-03-B	1-07-B	2-07-B	1-10-B	2-20-B	2-22-B	
Me-Benzonaphthothiophene	-	406.5	-	-	-	-	-	A1
Unknown S	-	408.3	-	-	-	-	-	
Me-Benzonaphthothiophene	-	418.9	-	-	-	-	-	A1
Me-Benzonaphthothiophene	-	420.9	-	-	-	-	-	A1
Unknown T	424.4	-	-	424.1	423.4	425.4	424.4	
Phthalate	-	-	-	424.1	423.4	425.4	424.4	A1
Unknown U	-	428.2	-	-	-	-	-	
Phthalate	-	428.2	-	-	-	-	-	A1
Me-228	-	430.2	-	-	-	-	-	A1
C_2-228	-	459.2	-	-	-	-	-	A1
Unknown V	-	-	-	-	-	464.1	-	
Unknown W	-	-	-	-	-	475.1	-	
Benzo(j,b,k)fluoranthenes	-	475.0	-	-	-	-	-	B,C
Benzo(e)pyrene	-	492.3	-	-	-	-	491.4	B,C
Unknown X	-	492.3	-	-	-	-	491.4	
Unknown Y	-	-	-	-	-	496.0	-	
Unknown Z	-	509.4	-	-	-	-	-	A1

1) EPA/NIH Mass Spectral Data Base, Heller and Milne (eds.), NSRDS-NBS 63 (1978).
2) Registry of Mass Spectral Data, Stenhagen, Abrahamsson and McLafferty (eds.), John Wiley & Sons (1974).
3) Calculated from data of Lee *et al.* (1979).

7. "FLAG" TABLES (SPECIFIC SEARCHES)

A. Search for Compounds > 50 ppb in Sediments

The information for this search is compiled in Tables 27a and 27b. The complete search lists are in Appendix IV. It confirms and expands in detail what has already been discussed of the bar graphs: that most organic pollutants are found in the upper Bay and that unsubstituted PNA's are the major contributors. Comparing Table 27a with Table 27b, one may be tempted to conclude that the samples collected in fall 1979 contain a more diverse set of compounds than those collected in spring. This, however, is not so as Table 20 indicates: it is an artifact of the cut-off at 50 ppb. In addition, Table 27b contains a number of compounds such as 4H-cyclopenthaphenanthrene, 2-phenylnapthalene, methyl-phenylnapthalene and one methyl-202 isomer that relate directly to the very large pyrogenic fraction encountered in sample 2-27-S. Again, Table 20 shows that they are also found in other samples but at levels < 50 ppb.

Sample 1-22-S contains 9-fluorenene, and sample 2-25-S contains two C_2 and two C_3-napthalenes, a C_2-biphenyl or C_2-acenapthlene isomer, dibenzothiophene and C_3-biphenyl/C_2-dibenzofuran. Again, many of these compounds have been identified in other samples at lower concentration. The high concentrations of relatively volatile compounds in sample 2-25-S could possible indicate contact with No. 2 fuel.

With few exceptions, maximum concentrations for different compounds were encountered near Baltimore Harbor (stations 22 and 23) or near the mouth of the Chesapeake-Delaware Canal (station 26) if sample 2-27-S is excluded from the discussion.

B. Search for New Compounds and for an Order of Magnitude Change in the Concentration of Specific in Individual Stations Between Spring and Fall (Sediment)

This search, like that for specific compounds (Figure 19 to 27), requires a definition of the retention window within which a compound must elute. Each ARI has a certain precision and error associated with it (Table 15). If the search window chosen is too small, the peak may not be recognized. On the other hand, if the window is too large, two different compounds may be recognized and compared as one. To minimize such mistakes, a strict quality control for the relative retention properties of capillary columns is necessary, and adequate standards for this purpose will have to be developed. Temporal searches, however, can never be perfect. They should point our attention to a situation that may require further investigation, but a critical review of the output is always a first step.

Table 27a

List of compounds $\geq$ 50 ppb (dry wt.) in sediment samples - Spring 1979. Stations in which no compound exceeded this lower limit are not listed.

Compound	ARI	Station 01	18	20	21	22	23	24	25	26
Fluorene	(151.0-152.4)					54	57			53
9-fluorenone+(C_2-168/C_3-154)	(191.0)					52				
Phenanthrene	(200)		57	127	235	365	464	303	87	360
Anthracene	(203.0-203.3)					63	74			68
Me-phenanthrene	(238.4)					68	63			50
Mixture	(260.7-261.1)			59	148	179	176	108		138
C_2-phenanthrene	(278.5)					56				
Fluoranthene	(285.5)	89	78	136	411	460	551	199	81	602
Acephenanthrylene	(292.3)									60
Pyrene	(300)	63	56	119	382	397	506	179	85	525
C_3-phenanthrene+...	(313.5-313.9)					58	50			55
Me-202	(330.1-330.4)				129	145	164	51		184
Me-202/Benzo(b)fluorene	(335.5-336.7)					126				188
Me-202	(365.8)				52		58			56
Me-202	(371.0-371.4)				80	67				67
Benzonaphthothiophene	(377.6)									51
C_2-phenanthrene	(380.1)						97			
Mixture	(388.3)								59	
Benzo(a)anthracene	(397.0)	58			161	107	230			263
Chrysene/Triphenylene	(400)	63		76	238	163	323		58	330
Me-228	(429.2-429.8)				71	51	84			106
Me-cyclopentapyrene+Me-228	(438.9)				55		55			
Unknown	(444.3-445.0)				51	82	57			140
Benzo(j,b,k)fluoranthenes	(473.3-474.9)			142					96	

Table 27a (continued).

Compound		01	18	20	21	22	23	24	25	26
Benzo(e)acephenanthrene	(479.7-480.9)						67			56
Benzo(e)pyrene	(489.9-491.4)				147	62	213			169
Benzo(a)pyrene	(493.2-494.7)				163	68	275			219
Perylene	(500)				149	144	313		419	1000
Indeno(1,2,3-cd)pyrene~~+~~m.w. 278	(577.9-578.5)			52	154	64	216			141
Dibenzo(def,mno)chrysene	(582.4)						53			81
Benzo(ghi)perylene	(600)				123		181			

Remarks:

In cases where substituted PNA's overlap in their retention and cannot be positively identified, Me- or C_2- is followed by the molecular weight of the unsubstituted compound. Thus, Me-202 could be Me-fluoranthene, Me-pyrene or Me-acephenanthrylene, Me-228 could be Me-benzo(a)anthracene or Me-chrysene/triphenylene, etc.

1) Identified by ARI only.

Table 27b

Listing of compounds $\geq$ 50 ppb (dry wt.) in sediment samples - Fall 1979.

Stations in which no compound exceeded this lower limit are not listed.

Compound	ARI	Station													
		3	8	13	17	18	19	20	21	22	23	24	25	26	27
C_2-Naphthalene	(109.7)												153		
C_2-Naphthalene	(114.6)												53		
C_3-Naphthalene	(147.5)												55		
Fluorene	(151.9 -152.1)									52	71				
C_3-Naphthalene	(153.4)												70		
C_2-Biphenyl/C_2-Acenaphthene	(165.4)												53		
Dibenzothiophene	(193.8)														5900
C_3-Biphenyl/C_2-Dibenzofuran	(194.5)												50		
Phenanthrene	(200)	60				63		102	240	314	439	153	114	155	95000
Anthracene	(203.3)														5200
Methylphenanthrene	(238.2)										52				
4-H-Cyclopenta(def)phenanthrene	(243.1)														9800
Methylphenanthrene	(244.2 -245.2)									174					8600
Mixture	(260.7 -261.2)								87	113	171	70		56	
2-Phenylnaphthalene															5100
Di-n-butylphthalate[1)]	(267.9)														53000
Fluoranthene	(285.4 -285.8)	64	60	60	75	73		100	250	288	522	138		206	180000
Pyrene	(300)	56	68		67	59		92	228	285	480	137		176	130000
Me-phenylnaphthalene+m.w.204	(303.7)														21000
C_3-phenanthrene+...	(313.7)										54				
Unknown[2)]	(327.8)														80000
Me-202	(330.2 -331.0)								72	120	146				5000

Table 27b (continued) (2)

Compound	ARI	Station 3	8	13	17	18	19	20	21	22	23	24	25	26	27
Me-202/Benzo(b)fluorene	(335.6 -336.8)								76	90	148			67	23000
Me-202	(345.8)														5900
Me-202	(365.9 -366.1)									52	60				
Mixture	(366.8)														
Benzo(ghi)fluoranthene +benzo(c)phenanthrene	(381.0 -381.9)									55					5500
Benzo(a)anthracene	(397.1)								107	108	228	56		97	47000
Chrysene/Triphenylene	(400)	54					224		138	173	322	90		99	68000
M.W. 228	(404.7)														9100
Me-228	(412.9)														5500
Me-228	(429.7 -429.9)									56	84				
Me-cyclopentapyrene+Me-228	(438.6)										60				
Unknown	(444.5 -444.6)									64	65			62	
Benzo(j,b,k)fluoranthenes	(473.9 -474.8)	57	86		89	71		101		336				207	22000
Benzo(e)acephenanthrylene	(480.7 -481.4)										56				7400
Benzo(e)pyrene	(490.4 -491.4)								84	107	187	51		62	49000
Benzo(a)pyrene	(493.4 -494.4)								113	133	238	60		90	73000
Perylene	(500)					63			112	316	289	205	536	419	24000
Me-252	(507.9)														5300
Unknown2)	(517.4)														8500
Me-252+m.w. 278	(521.0)														9000
Hopanoid	(541.5)													56	
C_2-252+m.w. 278	(541.7)														5000

Table 27b (continued) (3)

Compound	ARI	Station 3	8	13	17	18	19	20	21	22	23	24	25	26	27
C_2-252+...	(548.7)														8200
C_2-252+...	(554.7)												96		
Mixture[2]	(564.5)														9500
Unknown[2]	(576.1)														13000
Indeno(1,2,3-cd)pyrene+m.w. 278	(577.9 -580.2)								78	99	155			69	53000
m.w. 278	(586.2)														11000
Benzo(ghi)perylene	(600)								69	81	136				43000

Remarks:

In cases where substituted PNA's overlap in their retention and cannot be positively identified, Me- or C_2- is followed by the molecular weight of the unsubstituted compound. Thus, Me-202 could be Me-fluoranthene, Me-pyrene or Me-acephenanthrylene. Me-228 could be Me-benzo(a)anthracene or Me-chrysene/triphenylene, etc.

1) Present only in chromatograms: since phthalates elute in the G2 fraction, all phthalates found in the G3 fraction must be considered to be contaminants.

2) Probably contamination - not present in GC-MS data.

The complete search lists are found in Appendix V. Only three examples have been selected for discussion here. There are two stations for which - based on discussion in a previous chapter - we already know what to expect. Station 2-19-S, because of the dramatic compositional change between spring and fall 1979, should contain a listing of mainly new compounds. A flag for a tenfold concentration increase, though, can be expected for compounds where retention coincidence within the search window occurs. The printout for this station is found in Appendix V. Of twenty-six compounds, sixteen are indeed listed as new (cutoff at 50 ppb) and ten indicate a concentration increase. If these ten are checked with the mass spectrometric output, it is immediately evident that only the first listing is accurate (ARI = 244.5, a compound with M.W. 192) and that others should be listed as new compounds. Although it has been said before, we state again that such coincidences in ARI's are a basic problem that cannot be avoided.

In the printout for station 2-27-S, the flag-list should indicate large concentration increases, especially for pyrogenic PNAs. Of the thirty-six compounds that are printed out (Appendix V), only eleven compounds are listed as increases, while the remaining are characterized as new compounds. However, one also notes that in every case where the new compound flag is raised, there is no entry for the spring sample. As was discussed previously, the spring sample consistd mainly of sand and the chromatogrm contained only a few peaks that passed the integration threshold. It also is possible that missing compounds are outside the adopted retention window. If there is no entry for a particular compound in one of the samples compared, this compound will be listed as new if the corresponding peak is missing in the earlier sample, or it will appear as a "> 10 x decrease" if it is missing in the later sample. Much of the apparent discrepancy is caused by the differences in the sediment character rather than the software.

As a third example, finally, we choose station 26-S. There are nine compounds flagged (Appendix V), most of which are indicating a concentration decrease while one compound at ARI 439.2 appears to increase.

A check in Table 20 indicates the presence of two different compounds with identical ARI (438.3) in sample 2-26-S, while there is no listing for sample 1-26-S. Thus, one would conclude from the mass spectrometry that the flag should indicate a new compound and not, as the search shows, a concentration increase. The discrepancy is caused by a small peak identified by the computer in the FID chromatogram of sample 1-26-S and falling within the range of the retention window for the search.

C. Search for Compounds > 50 ppb in Oyster Tissue

Tables 28a and 28b contain a summary of the computer printouts for this search. Appendix VI gives the complete listing. It is immediately evident that the data for the spring cruise contain very little relevant information: only dibenzothiophene, 2-phenylnaphthalene and a C_2-dibenzothiophene in station 10, and fluoranthene in station 22 are pollutants with concentrations > 50 ppb. Methyl tetradecanoate and methyl

TABLE 28a

List of compounds > 50 ppb (dry weight) identified in oyster samples - Spring 1979

Stations in which no compound exceeded this limit are not listed.

		Station																
Compound	ARI	05	06	07	08	09	10	11	12	13	14	15	17	18	19	20	22	23
Unknown F_1	104.2						106											
Unknown H	138.1-141.6			477	104		144		158		138	246		98	262	52	105	97
Unknown (H_1+J+K)	158.0-159.0						56	86										
Unknown	161.5*						51											
Unknown	164.6*					53												
Methyl Tetradecanoate	191.1-193.5			166			136											
Methyl Hexadecanoate	251.4			133														
2-Phenylnaphthalene	255.6						87											
C_2-Dibenzothiophene	265.2						73											
Fluoranthene	285.2																63	
Contamination	327.6							53										
Contamination	359.6							59										
"	384.5							51										
"	386.7-387.2							103		150								
Unknown	391.7*						53											
Contamination	413.0-413.5							137		188								
"	425.7													58				
Unknown	429.9*						55											
Contamination	438.1-438.4					50		169										
Contamination	462.1							199							61			
"	483.5-485.4		50			57		195		179			64		69			
"	490.5													94				
"	517.0						72											
"	531.7-533.0	51	65			59		189	62	162		57	100	59	75			
"	560.8-561.5							117					82					
"	572.6						103											
"	594.2-597.1		51			54		144	62		57		103	55	65			

*Peak did not show up on MS

Table 28b

List of compounds > 50 ppb (dry weight) identified in oyster samples - Fall 1979

Stations in which no compound exceeded this limit are not listed.

Compound	ARI	Station 01	03	05	07	09	11	13	14	15	16	17	18	20	21	22
Unknown (F1 + F2)	101.4															66
Unknown G	107.4															56
Unknown H	137.5-139.9				144					188	141	64	213		54	68
Unknown K	156.7-157.5		227										61			
Methyl Hexadecanoate	242.3-243.9			83												58
Phthalate	253.3-255.5				70	51	55	51	75	86			74		59	50
C_2-Dibenzothiophene	260.6		111													
C_2-Dibenzothiophene	267.2		61													
C_2-Phenanthrene	273.4	79														
Unknown M	277.3-277.8		65		159	180	169		54							
C_2-Phenanthrene/ C_3-Dibenzothiophene	281.4		59													
C_3-Dibenzothiophene/ Fluoranthene	283.3-284.8		104	152												72
C_3-Dibenzothiophene	288.6		93													
C_3-Dibenzothiophene	294.6		59													
Unknown	298.3-298.9		138	64												
C_3-Dibenzothiophene	307.5		98													
C_3-Dibenzothiophene	311.4		77													
C_3-Phenanthrene/ C_3-Dibenzothiophene	314.2		82													
Unknown Q	366.6															60
Unknown R	392.5-393.9													52	72	55
Unknown	397.4			67												
Unknown	473.0			51												
Unknown (m.w. 366)	495.4													50		
Unknown	519.1													88		
Unknown	542.2													83		
Unknown	564.8													77		
Unknown	592.1													70		

hexadecanoate are of known biogenic origin. Unidentifiable compounds of probable biogenic origin are also present. Beginning with ARI 327.6, there are a series of peaks that did not show up in the GC-MS analyses and for this reason could not be identified. Their presence in the gas chromatograms only suggests that they are lab contaminants.

Compound-identification Table 26 indicates the presence of other pollutants, among them p,p'-DDE and some unidentifiable chlorinated hydrocarbons. Since they are not listed in the flag tables, they have concentrations < 50 ppb.

The data for the fall cruise are similar to those for the spring 1979 cruise, except that a larger variety of substituted dibenzothiophenes appears to be present at levels > 50 ppb in station 03. Station 03 also clearly stands out in Table 26 and for this reason deserves further discussion. A closer examination of the compositional details reveals that higher substituted naphthalenes, fluorenes, dibenzothiophenes and phenanthrenes abound. These features find a common denominator in surface oil slicks after prolonged exposure. In addition, there are some chlorinated compounds present whose structure cannot be identified. Since the oyster samples for the second cruise were collected by boat from pilings of the Hampton Roads Bridge Tunnel, it is not unreasonable to suspect that these oysters indeed could have been exposed periodically to surface oil slicks. Two possible explanations can be offered for the seasonal differences. First, cool wintertime temperatures inhibit oyster pumping rates, reducing probability of contact with polluted water. Second, fall-collected oysters may have been exposed to oily water before their collection and simply had less time to depurate.

D. Search for New Compounds and for an Order of Magnitude Change in the Concentration of Specific Compounds in Individual Stations Between Spring and Fall (Oyster)

As for sediments, the complete search list is attached in Appendix VII, and only a few stations will be discussed here. In general, the search indicates a concentration decrease and few new compounds appearing for all stations except 03, where the first two listings indicate a concentration increase. In view of the discussion of this station in the preceding chapter, the reasons for this exception are trival. The same is true for stations which indicate concentrations > 50 ppb in spring but contain no listing for fall: those are compounds that likely entered the chromatograms as lab contaminants. The exception is fluoranthene in station 22 which is listed twice, first at ARI 283.3 as a "new compound" and the second time at ARI 285.2 as a "> 10 x decrease." This problem is due to the retention index window difficulties that were discussed in the previous chapter.

One may correctly conclude that the temporal search for oysters is not very fruitful. But the reasons are understood and the problems can be corrected if more attention is paid to details and stricter quality control procedures are employed for the gas chromatography.

CONCLUDING REMARKS

Monitoring the environment for the presence of toxic organic compounds in a routine fashion is unlikely to be perfect in every respect. The methodology developed under this grant emphasized an unbiased approach in which a large variety of organic compounds is extracted and analyzed. Extensive use of computers was employed, not only for cutting the cost of such analyses but also to improve them. Contrary to this, any biased approach would have to incorporate methodology narrowly tailored to specific compound properties which would have to be known in advance. Not only would the number of compounds that can be analyzed by such methods be very limited, but the probability of some unexpected pollutant being detected would be a low. Any attempt to cover a wide variety of organic compounds by such methods would require multiple extractions, separations and analyses, which would make it too time-consuming and expensive.

In this project, much emphasis has been directed towards a reliable interpretation of GC analyses to avoid the high costs of GC-MS analyses. The analytical scheme as presented here correlates the detailed information from GC-MS anlayses to GC chromatograms with the help of specialized retention indices. One of them, the aromatic retention index (ARI) first proposed by Bieri (1977), was extensively used and tested. While it is not a perfect substitute for a GC-MS analysis, its application is indeed very powerful insofar as it for the first time allows a precise definition of most peaks in the chromatograms and thus their defined storage in a computerized data bank which can be addressed for inquiries any time in the future. There is a good correlation between the GC and the GC-MS data where they both have been compared.

As we have discussed, inconsistencies can occur where two or more compounds have ARI's that coincide within the error attached to an ARI determination. This is a basic problem that cannot be easily solved. Inconsistencies can also occur due to differences in the liquid phase, caused in the manufacture of glass capillaries, or by aging. Strict quality control during manufacture and use is indicated. There also still are some flaws in existing software for the recognition and integration of peaks in cases of insufficient resolution and in the presence of a large UCM. More refined programming certainly is advised.

A substantial effort will be needed to determine suitable retention standard relationships between aromatic index markers and other compound types. As was mentioned in the discussion of oysters, methyl esters of fatty acids are not well-defined by aromatic retention standards. The use of pesticide retention standards failed not in principle, but because the

E.C. detector also responds to many PNA's and other organic compounds. Additional efforts are needed to solve this problem.

There is some reason for dissatisfaction with the HPLC separation employed throughout the program. Since the GPC fractions underwent a solvent change from CH_2Cl_2 to toluene during concentration, the initial conditions for the high performance separation were affected by the presence of the toluene. This resulted in some separation problems that by proper design can be corrected.

Finally, one needs to readdress the sedimentological characterizations of sediment samples. As long as the sediments to be extracted and analyzed are very similar, there is no problem. But if they vary as dramatically as they did in the Chesapeake Bay, from sand to clay, the sedimentological composition cannot be neglected. We tried to correct this problem by normalizing the organic data to silt/clay in a first approach. Such a solution, however, is unsatisfactory insofar as samples consisting almost of pure sand do not contain high enough concentrations of organic compounds to allow analysis, so a normalization cannot be carried out. An alternate solution probably would be to separate and collect the silt/clay fraction from a sandy sample and perform an extraction on the fines only. How this could be achieved without contaminating the sample and without also taking out some organic detritus is not yet clear.

REFERENCES

Bieri, R. H., 1977. Middle Atlantic Outer Continential Shelf Studies, Vol. II-B, Section II. Report to the BLM by the Virginia Institute of Marine Science, Gloucester Point, Va.

Bieri, R. H., M. K. Cueman and C. W. Su, 1978. An Aromatic Retention Index Scale. Presented at the 30th Southeastern Regional Meeting of the ACS, Savannah, Ga.

Bieri, R. H., M. K. Cueman, C. L. Smith and C. W. Su, 1978. Polynuclear Aromatic and Polycyclic Aliphatic Hydrocarbons in Sediments from the Atlantic Outer Continental Shelf. Intern. J. Environm. Anal. Chem., 5, pp 293-310.

Bieri, R. H., M. K. Cueman, R. J. Huggett, W. MacIntyre, P. Shou, C. W. Su and G. Ho. Investigation of Organic Pollutants in the Chesapeake Bay. Report of May 15, 1979, to the E.P.A./Chesapeake Bay Program, Annapolis.

Byrne, R. J., C. H. Hobbs III, M. J. Carron, 1982. Draft Final Report, Baseline Sediment Studies to Determine Distribution, Physical Properties, Sedimentation Budgets and Rates in The Virginia Portion of The Chesapeake Bay: Virginia Institute of Marine Science, 200 p.

E.P.A./NRDC Settlement Agreement.

Grimmer, G., and H. Bohnke, 1972. Bestimmung des Gesamtgehaltes aller Polycyclischen Aromatischen Kohlenwasserstoffe in Luftstaub and Kraftfahrzeugabgas unit der Capillar-Gas-Chromatographie. Z. Anal. Chem. 261, pp 310-314.

Grimmer, G., K. W. Naujack and D. Schneider, 1979. Changes in PAH-Profiles in Different Areas of a City during the Year. Polynuclear Aromatic Hydrocarbons. A. Bjorseth & A. D. Dennis, Ed, Battelle Press, Columbus, Ohio.

Grob, K., Jr., G. Grob and K. Grob, 1978. Comprehensive Standardized Quality Test for Glass Capillary Columns. J. Chromatogr., 156, pp 1-20.

Grob, K., and G. Grob, 1979. Deactivtion of Glass Capilaries by Persilylation. J. HRC&CC, 2, pp 677-678.

Godefroot, M., M. Van Roelenbosch, M. Verstappe, P. Sandra and M. Verzele, 1980. High Temperature Silylation of Glass Capillary Columns. J. HRC&CC, 3, pp 337-344.

Giger, W., and M. Blumer, 1974. Polycyclic Aromatic Hydrocarbons in the Environment. Isolation and Characterization by Chromatography, Visible, Ultraviolet and Mass Spectrometry. Anal. Chem., 46, pp 1663-1671.

Hein, C., 1980. Interpretation of GC-MS Data by Reverse Search and Relative Retention Indices. Thesis, Virginia Institute of Marine Science.

Heller, S. R., G. W. A. Milne, 1978. EPA/NIH Mass Spectral Data Base. U. S. Dept. of Commerce/National Bureau of Standards, Washington, D.C.

Hites, R. A., R. E. Laflamme and J. G. Windsor, 1980. Polycyclic Aromatic Hydrocarbons in Marine/Aquatic Sediments: Their Ubiquity. Adv. Chem. Ser. 185.

Laflamme, R. E., and R. A. Hites, 1978. The Global Distribution of Polycyclic Aromatic Hydrocarbons in Recent Sediments. Geochim. et Cosmochim. Acta, 42, pp 289-303.

Lao, R. C., R. S. Thomas and J. L. Monkman, 1975. Computerized Gas Chromatographic Mass Spectrometric Analysis of Polycyclic Aromatic Hydrocarbons in Environmental Samples. J. Chromatogr. 112, pp 681-700.

Lee, M. L., G. P. Prado, T. B. Howard and R. A. Hites, 1977. Source Identification of Urban Airborne Polycyclic Aromatic Hydrocarbons by Gas Chromatrographic Mass Spectrometry and High Resolution Mass Spectrometry. Biomed. Mass Spectr., 4, pp 182-186.

Meislich, H., H. Nechamkin and T. Sharefkin, 1977. Organic Chemistry McGraw-Hill Co, New York.

The Merck Index, 1976. 9th Edition. Merck & Co., Inc., Rahway, New Jersey.

Oak Ridge National Laboratory, 1979. Identification and Quantification of Polynuclear Organic Matter (POM) or Particulates from a Coal-fired Power Plant. EPRI EA-1092, Project 1057-1, Electric Power Research Institute, Palo Alto, Calif.

Peterson, J. C. 1980. Analysis of Phthalate Esters in Chester River and Chesapeake Bay Sediments. Dissertation, U. of Maryland.

Wise, S. A., S. N. Chesler, H. S. Hertz, L. R. Hilpert, and W. E. May, 1977. Chemically Bonded Aminosilane Stationary Phase for the High Performance Liquid Chromatographic Separation of PNA Compounds. Anal. Chem., 49, pp 2306-2310.

Nichols, M. M., R. Harris, G. Thompson and B. Nelson. 1982. Metal Inventory and Fate of Suspended Sediment in Chesapeake Bay. Special Scientific Report No. 106, Va. Inst. of Marine Science.

Pflugmacher, J. and W. Ebing, 1978. Zur Kenntnis des Evolutionsverhaltens einiger Pflanzenschutzmittel. J. Chromatogr., 151, pp 171-197.

Stenhagen, E., S. Abrahamsson, F. W. McLafferty, 1974. Registry of Mass Spectral Data. John Wiley & Sons, N.Y.